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QUARTERLY REVIEW

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VOL. XIX JANUARY, 1933 No. 9

PROTECTIVE VALUE OF ELECTROPLATED METAL COATINGS ON STEEL

PROGRESS REPORT

By the Joint Inspection Committee of the American Electro-Platers Society, American Society for Testing Materials, and Bureau of Standards

This Committee consists of:

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I. Introduction

The purpose of this report is to summarize the results of the exposure tests of electroplated coatings on steel up to October 1, 1932, and the progress made in the study of accelerated tests. This discussion is confined to samples with nickel or chromium finishes. There have not been sufficient failures of zinc or cadmium coatings to warrant any conclusions, and no laboratory tests have yet been made on these coatings.

As the following conclusions for nickel and chromium coatings are based on from six to eight month's exposure, during which time extensive failures occurred in only three locations, *they must be considered as tentative* and subject to revision in the light of future observations. Some of the results are so striking, however, that it is believed by the Committee that they warrant publication at this time. The Committee will be glad to receive comments and especially and definite evidence that appears to contradict or modify these conclusions.

II. Conditions Used in the Exposure Tests and Inspections

The details of the preparation of the specimens have been published in a mimeographed report, and in the May, 1932 Monthly Review of the American Electro-Platers Society. Five specimens of each set were exposed as follows: Washington, D. C. and Key West, Florida in February, 1932, and New York, N. Y., Sandy Hook, N. J., Pittsburgh, Pa., and State College, Pa., in April, 1932. They have been inspected at intervals of about one month by members of the Committee, assisted in many cases by other interested persons. In all 44 inspections have been made, with a total of 142 persons participating, or an average of over 3 per inspection. The Committee desires to thank all those who have aided in these inspections. All persons desiring to take part in an inspection are welcome. Dates will be furnished on request addressed to the Chairman of the Committee.

At each inspection, each person gave a numerical rating to each specimen, based upon the presence and extent of rust, in accordance with the following scale:

Rating No.	*Approximate per cent of area rusted*
5—Perfect, no rust	0
4—Very slight rust	0– 5
3—Slight rust	5– 10
2—Decided rust	10– 20
1—Very evident rust	20– 50
0—Badly rusted	50–100

Rust within ¼ inch of the edges of nickel or chromium samples was disregarded, as the edges may have been buffed through. Rust stains extending more than ¼ inch from its apparent origin were also disregarded. Defects other than rust, such as white or dark stains, blisters, etc., were noted, but did not enter into the numerical ratings.

The behavior of the five specimens in each set was remarkably uniform. In general the ratings of different inspectors were in good agreement, but in a few cases the results were less concordant. Such difficulties arose chiefly on samples that were very dark, and on which rust may or may not have been present. Subsequent inspections sometimes clarified these discrepancies. In all cases the mean of all observations was recorded and used in the computations.

After each inspection, the mean rating (R) for a set was recorded, and the average of this and the preceding mean value

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was multiplied by the number of weeks between inspections, to give the score (S) for that period. If for example at one inspection (R) was 3.0 and 4 weeks previously (R) was 3.5, the average rating was 3.25 and the score was 4 x 3.25 = 13. If the previous score was 47, the total score (T) was 47 + 13 = 60. If the total period was 16 weeks, the total score of perfect samples would have been 16 x 5 = 80. The score of 60 for this set therefore represents 60/80 = 75% (T%) of a perfect score. The following tentative conclusions are based on the percentage scores up to October 31, 1932. Differences of less than 10% in these results are probably not significant.

The rate of failure depended upon the character of the coating and upon the location. In general, most rapid failure occurred in Key West, Sandy Hook and Pittsburgh, and least rapid in Washington and State College, with New York intermediate. This is shown in Fig. 1 for Set 52, with one-quarter thousandth (0.00025) inch of nickel. In this and corresponding figures, each small rectangle represents the average rating for an inspection period, multiplied by the length of that period. The total area of each figure therefore represents the total score. The ratio of this area to that of a corresponding rectangle with a height of "5", represents the percent score for the period.

The relative rates of corrosion of different sets in a severe location (Key West) are shown in Fig. 2. Those figures with a shaded strip on the right represent sets that have failed completely while the other tests are still in progress.

III. Tentative Conclusions

The following conclusions are based on the average of the percentage scores in Key West, Pittsburgh, and Sandy Hook, where the corrosion was severe. In the other locations, the very thin coatings have failed but most of the samples are still so nearly perfect that it is not possible to draw valid conclusions at the present time.

1. Thickness. The most striking effect is that of the thickness, as shown in Fig. 3. With either pure nickel (Curve A) or with layers of nickel, copper, nickel (Curve B) very little protection was obtained when the total thickness was less than one-half thousandth (0.0005) inch, and good protection was not obtained unless at least one thousandth (0.001) inch was present.

2. Effect of Copper. The fact that Curve B (Fig. 3) is at all points below Curve A, shows that a coating containing layers of both copper and nickel has less protective value than a pure nickel coating with the same total thickness. In these experiments a coating containing copper and nickel had about the same protective value as a pure nickel coating with a thickness equal to that of the nickel present in the composite coating. This applies not only to deposits consisting of nickel, acid copper and nickel, but to all coatings containing copper, whether deposited from acid or

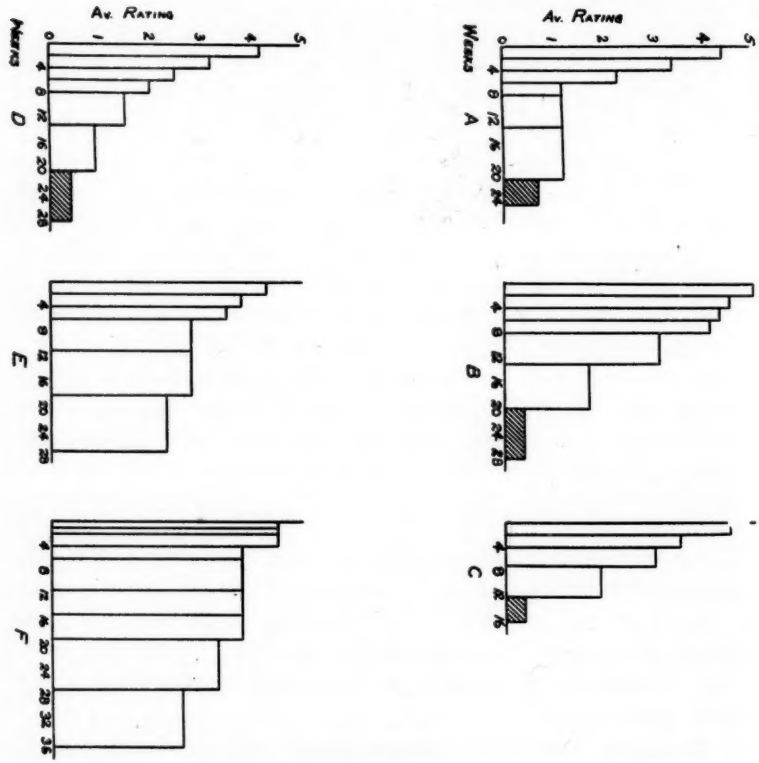

Fig. 1—Scores of Set 52 (0.00025 inch Ni)

	Location	*Total Score*
A	Key West	25
B	New York	46
C	Pittsburgh	24
D	Sandy Hook	28
E	State College	57
F	Washington	69

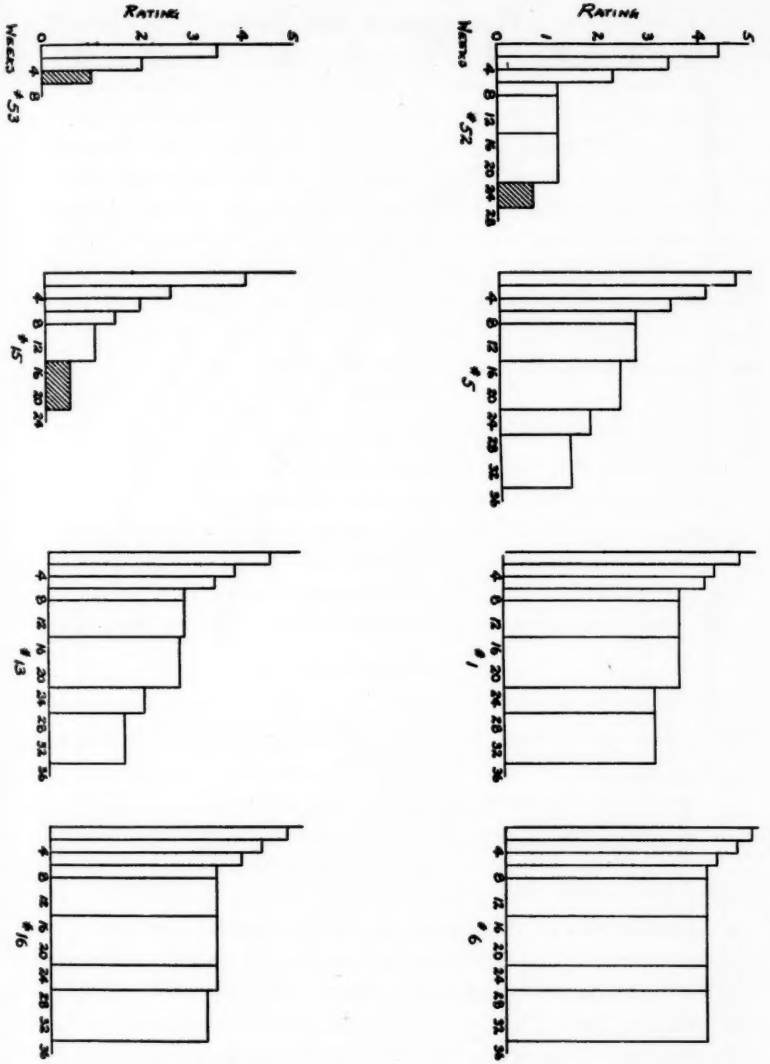

Fig. 2—Scores in Key West

No.	*Coating*	*Total Thickness In.*	*Total score %*
52	Ni	0.00025	25
5	Ni	.0005	49
1	Ni	.001	69
6	Ni	.002	81
53	Ni,Cu(A),Ni	0.00025	8
15	" "	.0005	17
13	" "	.001	49
16	" "	.002	68

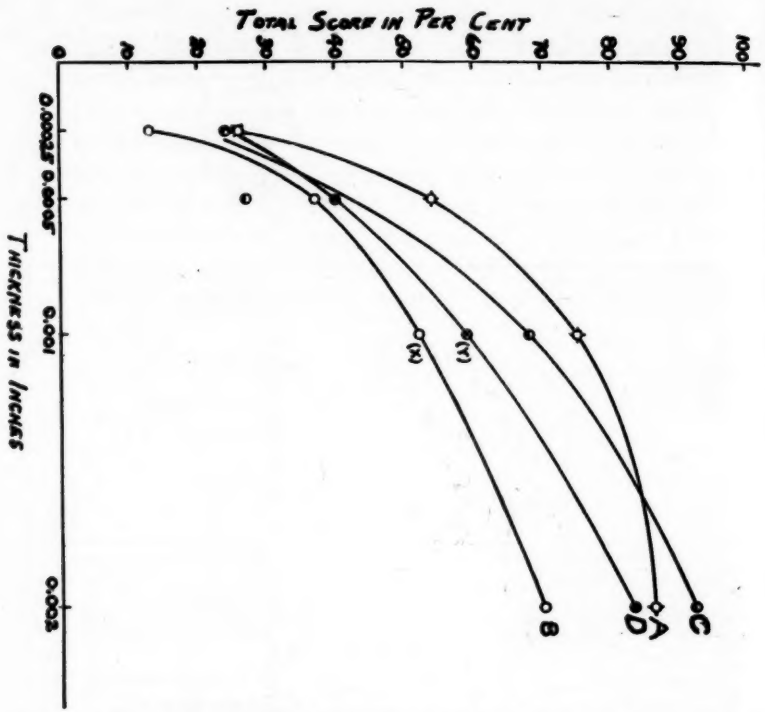

Fig. 3—Effect of Thickness of Deposits. Based on Average of Scores in Key West, Pittsburgh, and Sandy Hook.
A—Nickel
B—Nickel, Copper (acid), Nickel
C—Nickel, Chromium (0.00002 in.)
D—Nickel, Copper, Nickel, Chromium (0.00002 in.)
X—Average of 9 sets containing copper and nickel
Y—Average of 9 sets containing copper, nickel and chromium

cyanide baths. The point X represents the average of nine such sets. If copper is employed, its use should be based on some manufacturing convenience, and not on its protective value.

3. Effect of Chromium. Curve C of Fig. 3 shows that the presence of two hundred-thousandths (0.00002) inch of chromium (deposited at 113°F and 150 amp./sq./ft.) slightly decreased the protective value of all deposits consisting of nickel only, except very thick ones. On the other hand, the chromium increased the value of the coatings containing both nickel and copper (Curve D). The chromium apparently counteracted the above effect of the copper. It

appears that if chromium is to be applied, almost as good results are obtained when the undercoat consists of copper plus nickel as when it is pure nickel.

Other observations showed that a very thin chromium deposit, for example one hundred-thousandth (0.00001) inch, decreased the protection furnished by the nickel and copper layers, while deposits of three hundred-thousandths (0.00003) inch or more of chromium furnished added protection. Further exposure tests are planned to determine whether in general a thickness of 0.00003 inch of chromium is superior to 0.00002 inch. Further observations are also required to determine whether the conditions of chromium deposition exert definite effects.

4. Other Effects. The observations to date show that the conditions under which the copper or nickel was deposited had no marked effects on the protective value. It was found that although a layer of zinc or cadmium before the nickel sometimes increased the resistance to corrosion of the steel, such metals have a tendency to cause white stains and blisters, especially when exposed to severe conditions.

IV. Accelerated Tests

A preliminary study was made of a large number of accelerated tests. It was found that to obtain consistent results it is necessary to have the nickel or chromium surface so clean that it is free from "water break". A simple way to accomplish this is to rub the surface lightly with a paste of pure, finely divided magnesium oxide, and rinse it thoroughly.

The most promising tests for specimens with a nickel or chromium surface appear to be the ferroxyl and the salt spray tests. It is not yet known, however, whether these or any other tests will yield in a short time results that are closely parallel with the atmospheric exposures. This will be determined by further studies, including the application of these tests to the reserve samples of the same sets as were exposed.

Methods of stripping metals to determine the weight and average thickness of the coatings are also being investigated.

V. Future Plans

It will require about a year to complete the laboratory tests of nickel and chromium finishes. It is expected that by that time

the exposure tests (including certain supplemental exposures) will warrant practically final conclusions on such coatings. The zinc and cadmium coatings will then be studied, and their exposure tests compiled.

As soon as conditions permit, a similar study will be made of plated coatings on other base metals, such as brass, aluminum, zinc and die castings. To complete this entire program it is desirable that these researches be continued for at least three years from date.

PEELING OF ELECTRODEPOSITED NICKEL

By Dr. E. A. Vueillenmier

Read at the Philadelphia Convention, 1932

This talk on the peeling of nickel plating is ancient history to some of you. I offered Dr. Lukens something red hot from the typewriter, a paper on the electrodeposition from ammoniacal copper solutions, but he thought this story would be preferable.

I am somewhat timid, of course, in speaking to electroplaters on this subject; it is all right to talk to college boys and girls about it, but when a person has spent only about twenty minutes in an electro-plating shop, for him to speak before a group of people who have spent twenty and thirty years there, it is rather presumptuous.

Way back in 1916, over at the University of Berne, Switzerland, we were attempting to do something that we didn't succeed in doing, something that remained for Dr. Blum and Dr. Roden to do at the Bureau of Standards. We were making a systematic study of the nature of the deposit that is obtained from various metals. We made a lot of observations, but we weren't able to do what Dr. Blum was able to do, to classify the observations. The time had come for us to plate out from nickel, and strange as it may seem to you, we had no nickel to use as a nickel anode. I rather think that any nickel that was in Switzerland at that time was being used for other purposes. We weren't able to get hold of any metallic nickel, but we had some nickel solution, so the obvious thing, of course, was to prepare a nickel anode from the nickel solution by plating out, using a platinum anode and a platinum cathode. The platinum anode was a thin sheet, and the next morning I noticed that this thin sheet of platinum was bent. It occurred to me, of course, that in putting the metal into the bath, I might have bent the metal accidentally,

but fortunately I repeated the experiment, being careful to note that the piece of platinum was perfectly straight, and the next morning it was bent. The next step in this study, was to attach a pointer to the bottom of the platinum cathode, a long, thin glass pointer, and then we were ready for business. We used our home made nickel anode, and this (showing small strip of metal) was our cathode, and turned on the current, and the thing happened that we expected to happen. The pointer moved. Immediately, as soon as we turned the current on, the pointer moved. There was a scale up here, and we could study the speed with which the pointer moved. As soon as the current was turned on, the pointer moved toward the right, and we found that the speed with which the pointer moved depended, of course, upon a variety of conditions. After we had plated out for twenty or thirty minutes, or for an hour or two, we reversed the current, and much to our satisfaction, the pointer moved in the opposite direction, proving of course, that the platinum foil had not been permanently deformed.

Now, of course, in those days nothing was known, or very little was known about pH, and the solutions that were used were rather haphazard, and there were all sorts of explanations for the peeling of nickel plating. The peeling of nickel plating was blamed by many people on hydrogen. So we thought we would find out what hydrogen would do to the "Contractometer" that had some nickel plated on it. So instead of using a solution of nickel sulphate, we used an electrolyte of dilute sulphuric acid, or dilute sodium sulphate. We had the platinum anode, and here the platinum cathode that had some nickel plated on it, and the cathode, of course, had been bent. We turned on the current, and of course the thing that we expected was this: We expected that since hydrogen was responsible for contraction, for peeling, we expected that hydrogen would make the pointer keep on going in the same direction that it had been going. But, much to our surprise, it did exactly the opposite. In other words, when you plated out hydrogen into this nickel, what happened? The pointer moved to the left instead of the right.

Then, of course, the question of iron in nickel plating baths. A number of years ago, Mr. Thompson down at the Bureau of Standards, made a very careful study of the effect of iron in nickel plating solutions. In those earlier days, of course, nickel anodes contained 6%, 8%, 10% of iron, and there were some

people who worried very much about the presence of iron in nickel plating solutions. Certain of the German investigators claimed that the reason why you had peeling was because of the iron. Mr. Thompson, down at the Bureau of Standards, carried out a very interesting series of experiments in which he added a definite amount of iron to his nickel plating solution and then he investigated the deposit; that is, he studied the deposit, and found out whether the nickel would peel. And the conclusion to which he came, (and he presented his results in New York some five or six years ago at a meeting of the American Electrochemical Society)—the conclusion to which he came, if I understood them correctly, were that the presence of iron need not necessarily cause peeling. We rather got the impression from what he said that iron in nickel plating solutions is not objectionable.

At that time, we had a contractometer set up at Carlyle, at Dickenson College, and we immediately proceeded to study the same solutions that Mr. Thompson was using. We studied them with the help of this little instrument. And we had reached the point, of course, where we knew a little something about pH. The earlier investigations had ignored the matter of pH entirely. We prepared a solution of nickel sulphate that was normal in nickel, and quarter molar, if I remember correctly, in boric acid, and adjusted the pH by means of sulphuric acid, dilute sulphuric acid. We prepared a solution that had a pH of 5.7, and with that particular instrument, in twenty minutes the pointer moved 5 m.m. We prepared a similar solution having a pH of 6.1, and in twenty minutes the pointer moved 4 m.m. Then we took the solution that had a pH of 6.1 and added a little bit of ferrous sulphate to it,—sufficient ferrous sulphate so that the solution contained one gram of iron per liter, and we tested it out with the contractometer. This solution was made by adding the ferrous sulphate to the solution having a pH of 6.1, and the pH dropped to 5.9. That is, the pH of these three solutions was practically the same, 5.7 to 6.1. We tested this solution containing the iron with the contractometer, and the pointer instead of moving four or five m.m. in twenty minutes, it just raced. It moved 26 m.m. That is, with the pure nickel solutions, you could barely see the pointer move, but when this little bit of iron, one gram per liter, was present, the pointer raced 26 m.m. in twenty minutes.

Now, this is the conclusion to which we came.—First of all, a word about other methods. We studied silver from the cyanide bath, and when you plate silver from the cyanide bath, the pointer likewise moves, that is, there is a slight tendency toward contraction. If you use a copper solution, cyanide copper for instance, or tartrate, the pointer moves, but very, very slowly. Ordinarily, when you plate from a nickel solution, the pointer moves fairly rapidly at first, and moves more and more slowly. Now, you might draw the conclusion that as you plate out nickel, you get a thicker and thicker cathode, and that that is what is responsible for the slowing up of the pointer. That is, in the first five minutes it will move so far, but after it has been running say from fifteen to twenty minutes, in that five minute period of course it moves less. Now you might easily get the impression that that is due to the fact that you have on top of your platinum (and by the way, the side away from the anode was coated with vasoline or some other insulating material)—you might get the impression that that slowing up of the pointer was due to the fact that you are now having to bend, in addition to the platinum, some nickel, and of course, that is true to a certain extent. But we found, for instance, that when we used an iron solution, that the pointer would move quite rapidly, but instead of slowing up, it would go faster and faster. We found that when we plated from a solution of copper sulphate containing sulphuric acid, that the pointer would move rather rapidly at first, but after perhaps two or three minutes would practically come to a standstill. Now, you know that when you plate copper from sulphuric acid solution of copper sulphate, that your deposit at first is dense and smooth and shiny, but gradually it becomes coarser and coarser, and as soon as you get a coarse deposit here, the contraction seems to cease.

Summarizing, then, this is our notion on the subject of the peeling of nickel plating. When you plate nickel from a solution, the nickel film that is plated out has a tendency to contract. Of course, if you are plating out on something thick, that tendency to contract will still be there, but if this material is thick, is rigid, as of course it would be if it is thick, it won't obligingly bend as this thin sheet of platinum bent, and the result will be that the nickel will peel. The extent to which this tendency is present will, of course, depend upon the nature of the solution. We believe, that it is very materially influenced by the presence

of iron. Now, it is true, of course, that Mr. Thompson did not get peeling in the presence of iron. He was unable to get the solution to cause a deposit that would peel. But where you have a thick piece of metal, you are plating nickel on it, you are using a pure nickel solution, there is a very slight tendency toward contraction. On the other hand, if your solution contains iron, there is a tendency toward contraction that is five times as great. Now, of course, if your nickel adheres, then of course there won't be any peeling. That, apparently, is the trick. If you can get adhesion, then you needn't worry so much about peeling. But the tendency for the metal to contract is there, in the presence of iron. We believe, that if your nickel is shiny, that that kind of nickel will have a tendency to peel. That is based upon not our wide experience as electro-platers, but based upon our studies with this little instrument; that if you want metal that does not tend to peel, the metal must be relatively coarse and not shiny. We believe, that you want to keep away from iron, and we believe, of course, that in order for you to get good adhesion, the surface to be plated must be perfectly clean.

On a number of occasions, I have mentioned this later point: (a perfectly obvious one, of course). We have here an instrument with the help of which we can measure the tendency to contract. The next thing that we need is an instrument that will measure the degree of adhesion. We have tried all sorts of things. As soon as somebody succeeds in devising an instrument comparable to the contractometer for measuring the degree of adhesion, then a lot of the troubles of the electro-plater, we believe, will be over.

INTERNATIONAL FELLOWSHIP CLUB SUBSCRIBERS TO A. E. S. RESEARCH FUND

The International Fellowship Club, organization of sales representatives in the electroplating and metal finishing equipment and supply field, has contributed $50.00 to the Research Fund of the American Electro-Platers Society, according to an announcement by Tom Trumbour, secretary of the Club.

The action was taken after a conference between C. L. Van Derau, President of the A. E. S. and Mr. Trumbour, who in turn consulted the present and past officers of the Fellowship Club, all of whom concurred in the action.

The present contribution to the Fund is in addition to the customary annual Fellowship Club donation, which for the past two years has amounted to approximately $100.00 a year.

RECENT FOREIGN ORIGINAL RESEARCH IN ELECTROPLATING

By M. deKay Thompson
Philadelphia Branch
Read at the Philadelphia Convention, 1932

The purpose of the present paper is to give a resume of some of the original work that has been done abroad in electro-plating during the years 1931 and 1932.

Chromium Plating

A. Koenig, of Karlsruhe, has a short article in the Zeitschrift fur Elektrochemie, Vol. 37, p. 718 (1931), on chromium plating on light metals, such as aluminum, magnesium, and alloys of these metals. This is a field that has not been sufficiently developed on account of technical difficulties. Attempts to harden nickel deposited on these light metals by a deposit of chromium have not produced reliable results, for while good deposits of nickel can be produced, it scales off when chromium is deposited on it. Although the coefficients of expansion of chromium and these light metals differ more than do those of light metals and nickel, good deposits of chromium can be made directly on aluminum alloys such as duralumin (aluminum with 3.5 to 5.5% Cu, Mg 0.5 to 0.8%, Mn 0.5 to 0.8%), lautal (aluminum with 4% Cu and 2% Si) and silumin (aluminum with 5 to 14% Si) etc., without an intermediate layer of nickel. The surface must, of course, be free from oxide and a little roughened. A very uniform etching can be produced by depositing a very thin layer of nickel and dissolving this with nitric acid. Other metals do not work so well for this purpose, for the etching is too severe. Samples of direct chromium plating on light metals were shown.

W. Pfanhauser and G. Elssner of Leipzig have an article beginning on page 874, Vol. 27 of the Zeitschrift f. Elektrochemie on the theory and practice of chromium plating. They first discuss the throwing power of chromium baths, which is surprisingly low considering that this bath conducts ten times as well as a nickel plating bath. Throwing power is largely dependent on the sulfuric acid content.

Next the question as to the cause of the frequent failures in chromium plating is taken up. One cause may be the nature of the metal to be plated. While not much has been published on this subject, experience has resulted in the practice of plating different metals at different temperatures, brass between 30 and

38 deg. C. (86 to 100 F.) and nickel and iron between 40 and 45 deg. C. (104 and 113 F.). On nickel deposits which have been made several days previously it is impossible to deposit chromium at all, even at the highest current density. The explanation for this was found by measuring the cathode potentials and current densities for old and for fresh nickel plate. The results are shown in Figure 1, where it is clear that the old nickel cathode has such a low overvoltage for hydrogen that the potential can not reach the potential negative enough for the chromium to deposit. Electrolytic grease removal did not help, but old nickel surfaces when pickeled could be chromium plated as well as new ones and the electrode potentials coincided exactly with a fresh nickel surface. A peculiarity of chromium is that it is usually impossible to plate parts of surfaces later that were not covered at the start. This is also due to the lower overvoltage of hydrogen on nickel, judging from the electrode potential curve given.

The fifth paper by E. Müller on the theory of chromium plating has appeared in Vol. 38, p. 205 (1932) of the Zeitschrift f. Elektrochemie.

The method of attacking the theory of chromium plating is to measure the potential difference between the cathode and the solution at different current densities, with different solutions and different cathodes, and from the current density potential curves so obtained to draw conclusions as to what is taking place. For example, it has been found that pure chromic acid is not reduced even to chromium oxide on platinum cathodes, but the current increases only when the more negative potential is reached at which hydrogen is evolved. To explain this, it has been assumed that the most minute initial current forms a diaphragm of a chromium oxide which prevents chromic acid from coming in contact with the cathode, but which does allow hydrogen ions to penetrate to the cathode and be deposited, on account of their smaller size. This diaphragm is insoluble in chromic acid, or it would immediately be destroyed, and it is, therefore, assumed to consist of chromium chromate with the molecules all orientated with the basic part turned towards the cathode and the acid part toward the anode. However, as soon as a small amount of other acids is added, the reduction to trivalent chromium takes place and the current rises before the potential necessary for the evolution of hydrogen is reached. Also brown streams of Cr_2O_3 are visible around the cathode. This is due to

the destruction of the diaphragm by the other acid, so that chromic acid can reach the cathode and be reduced. The acid is not able to destroy the diaphragm alone, however, but this takes place only when a certain cathode potential has been reached. In order to explain this, it is assumed that no acid can attack the diaphragm until its molecules have penetrated to a certain distance in its pores and this force is greater the greater the cathode potential difference. The smaller the acid anion the less will be the potential difference required to make it follow the hydrogen ion and penetrate the diaphragm the distance necessary to destroy it, and for this reason the attack takes place at different potentials with different acids. In the case of the large anions, $HCrO_4$ and H_2PO_4, hydrogen is deposited at a potential difference which is not great enough to drag these large anions into the diaphragm.

Metallic chromium will also not deposit from pure chromic acid, while it does in the presence of sulfuric acid or sulfates. The diaphragm described above is responsible for this also, by keeping the chromic acid away from the contact with the cathode. The attack on the diaphragm by the small amount of other acid allows chromic acid to reach the cathode and be reduced to chromium. The potential necessary to deposit chromium is greater (more negative) than that required to reduce to trivalent chromium, but there is so much polarization for the reduction to trivalent chromium, that at high current densities the potential has to reach the value necessary for chromium deposition. The current density-potential curves on different metals are different up to the point where chromium begins to deposit, after this they are nearly coincident.

There is not time to review the many other details described in this paper.

Bernhard Planner, of Berlin, has a long article in the Zeitschrift fur Elektrochemie, Vol. 37, p. 33 (1931), on cadmium as a protection against rust, which is a review of what is known about the protecting properties of cadmium followed by an account of some of his own experiments on the deposition of cadmium.

In former years cadmium was considered a rather poor protection against rust, but recently this has been found to be wrong and it is now known to give good protection and adheres well to the underlying metal. This protective property is probably due to a thin film of cadmium oxide. A cadmium surface does not

keep a brilliant polish when exposed to the air, and must be laquered if a permanent high polish is desired. Cadmium alloys easily with many metals and may be completely absorbed by the underlying metal, but this alloy also protects the metal from corrosion. In the Udylite process this alloying is hastened by raising the temperature to 200°C, which results in a hardening of the protecting layer. Cadmium is used as a preliminary coating on iron for subsequent nickel or chromium plating. Cadmium is attacked appreciably by alkalis, but much less by acid than zinc.

Systematic investigations of the deposits from different solutions as to the current efficiency, protecting power, the required minimum thickness, and the physical character of the deposit, have not been made previously.

Cadmium can be deposited from both acid and from cyanide solutions. The cyanide baths have good throwing power and the metal is deposited in fine grains.

In these experiments cadimum was deposited on iron. It was not found possible to deposit a well adhering layer directly on aluminum.

Deposition from Cyanide Baths

In cyanide baths the grain size was found to increase with the temperature but not with the current density. The current efficiency was always increased by an increase in temperature, but lowered by an increase in current density. Summarizing for cyanide baths, the best conditions are: current density between 50 and 100 amperes per square meter (4.7 to 9.3 amperes per square foot), and between 40 and 60 deg. C., (104 and 140 deg. F.) The current efficiency is between 95 and 100%, and the appearance of the deposit was satisfactory.

Deposition from Acid Baths

Since sulfate and chloride baths are known to give markedly crystalline deposits, these experiments were carried out in solutions of cadmium fluosilicate, perchlorate, and phenolsulfate. In neutral fluosilicate the deposit is partly spongy. The crystals are in general larger than in the cyanide bath, and here also increased in size with the temperature and with the current density. Colloidal addition agents increase the current efficiency. The addition of licorice-extract produces very fine grained, dense deposits, but this is of no practical value for the deposit suddenly

turns spongy without any apparent cause. The addition of enough acid to make 0.05 normal prevents the sponginess, but then the licorice does not improve the deposit.

In all the acid baths the current efficiency increases with the temperature, and contrary to the cyanide baths also with increasing current density.

Perchloric acid baths do not wet the cathode well, consequently the deposit comes down only in spots. When the acidity is 0.05 to 0.10 normal, very coarse crystals are deposited (0.002 inch in diameter). The presence of a colloid reduces the crystal size to one fiftieth of this and when phenol is also present the crystal size is still smaller, but the current efficiency is not so good and the deposit is discolored. The current efficiency is affected by temperature and current density in the same way as in fluosilicate baths.

Neutral phenolsulfonate baths and those containing free acid up to 0.1 normal give spongy deposits. The presence of substances which increase the capillary attraction of the solution give satisfactory deposits with high current efficiency.

Various methods have been found to give polished deposits but they are all brittle and peel off.

The results of salt spray test on iron, protected by a layer of cadmium 0.00008 to 0.00014 inch thick compared with zinc of the same thickness, showed that cadmium lasted three times as long. Cadmium was found by other tests to be free from pores.

S. Wernick, of London, has an article on "Factors that Affect the Protection by Cadmium against Rust" in the Zeitschrift f. Elektrochemie, Vol. 37, p. 815 (1931).

Attention is called to the fact that cadmium and iron are only 0.1 volt apart in the electrolytic series so that if iron is exposed, cadmium deposited on iron would not be dissolved as rapidly as would zinc, which is 0.4 volt more negative than iron in the electrolytic series. It should, therefore, give protection for a longer time.

The three most important factors which determine the extent to which cadmium acts as a protection against rust are:

1. The nature of the underlying metal
2. The thickness of the deposit
3. The conditions under which the deposit is made

1. There may be slight differences in the potentials of various kinds of iron, which would affect the protective power of cadmium. Besides this, the physical properties of the underlying metal have an effect on the protection afforded. Rolled metal is in general preferable to cast, and soft steel to high carbon steel. Also freedom from slag and oxide inclusions is necessary for good results.
2. It is recommended that the removal of grease be done by electrolyzing as cathode in an alkaline solution to which a little cadmium cyanide is added to give a thin preliminary layer of cadmium. In the final plating, the smallest possible crystal size is desired, and cyanide baths give this.
3. It is important to determine the thickness of deposit that gives effective protection and still not exceed a reasonable factor of safety, because cadmium is relatively expensive. Of course this thickness will vary with the conditions of corrosion, that is, the climate in which it is exposed. If the average rate of atmospheric corrosion is calculated under the most unfavorable assumptions, the result is 0.00039 inch a year, corresponding to 0.850 g/dm^2 (0.28 oz./ft^2).

Cadmium deposits that are not treated in some way after the deposition, do not have a pleasing appearance after exposure to the atmosphere for some time. Indoors cadmium protects itself with a thin layer of oxide. From his own experiments the author states that the minimum allowable thickness of cadmium deposit is 0.0003 inch (0.0075 m.m.), which is 0.2 oz./ft^2 (0.6 g./dm^2). This minimum allowable thickness is determined by plotting the time required for the first appearance of rust in a corroding solution against the thickness of the deposit. The minimum thickness is that at which there is a sharp change in the direction of this curve, as it shows a sudden change in the rate of corrosion.

Planner's statement that cadmium deposits of 0.0025 m.m. (0.0001 in.) and more are not porous is disputed because Planner's method of testing for porosity was the appearance of blue spots when treated with potassium ferricyanide, but this does not work when the iron is covered with a more electronegative metal.

H. Krause has a paper in the Zeitschrift f. Metallkunde, Vol. 23, p. 283, (1931) on methods of coloring cadmium deposits. First the usual coloring baths used for other metals were tried,

without success. Finally, a successful coloring was obtained with a solution of 60 gr. of potassium chlorate and 125 g. of copper sulfate in a liter of solution. This solution is used to color zinc, a metal similar to cadmium. The operation of this pickle depends on the deposition of copper which is then oxidized to cuprous cupric oxides. Copper chloride gives better results than sulfate, and nitrate better than chloride. The best results were obtained with the following solution: 60 g. potassium chlorate and 35 to 40 g. of copper nitrate in a liter. This gives a deep black well adhering layer, when used at ordinary temperatures. Sodium chlorate works well as potassium. In order to get a brown color the following pickle can be used, although it does not work as well as the black: 10 to 15 g. of copper nitrate and 2.5 g. of potassium permanganate in a liter. This solution must be used near the boiling temperature for a longer time. A uniform brown color is obtained only after buffing dry with a soft brass brush. With more concentrated solutions the color is black, but only in hot solutions. A dark brown can be produced if copper carbonate is suspended in the solution.

These copper compounds reduced the protective property of cadmium and attempts next were made to color with cadmium compounds for example, the brown cadmium oxide and the yellow sulfide. Various solutions were tried, but success was obtained only with potassium permanganate and cadmium nitrate. The additions of iron chloride reduced the time and the amount of permanganate required. The deepest red brown color was given by the following solution: 320 g. potassium permanganate, 100 g. cadmium nitrate, 20 g. ferric chloride and a few drops of nitric acid in a liter.

Attempts to deposit well adhering deposits of cadmium sulfide were not successful.

Corrosion tests showed that the black coloring reduced considerably the protection against rust. The brown coloring with cadmium oxide had no effect.

R. Weiner, of Vienna, has an article on copper plating on aluminum in the Zeitschrift f. Elektrochemie, Vol. 37, p. 349, (1931). He says that copper plating aluminum might have some practical importance when copper is to be used as a preparation for plating with noble metals, or as a preparation for soldering. The aluminum surface should be slightly roughened in order to

make the deposit adhere well. This may be done by a sand blast or by etching. The following etching process has been recommended: a preliminary pickle of 10% sodium hydrate saturated with sodium chloride in which the aluminum is placed until a uniform evolution of gas takes place on the surface. It is then washed with water, dipped in a 2% hydrochloric acid solution, and then washed with water. Then for the purpose of roughening, it is electrolyzed as anode for 2 minutes in monochloracetic acid solution between one half and one normal, with a current density of about 250 amperes per square foot (25 amperes per square decimeter) at 60 volts, when the distance between the carbon anode and the cathode is 2.3 inches. The oxide later thus formed is removed by dipping for 10 to 20 seconds in a solution at 90 deg. C. (194°F.) of 23 grams of sodium carbonate and 45 grams of sodium bicarbonate in a liter. After washing, the object is placed in a 10% neutral copper sulfate solution and is plated for one hour with a current density of 10 amperes a square foot, or for two hours at 5 amperes a square foot in a solution of 22 grams of copper cyanide, 30 grams of sodium cyanide and 15 grams sodium carbonate in a liter.

The deposit could be buffed to a high polish and adhered so well that the aluminum sheet could be bent back and forth until it broke without loosening the deposit.

Experiments were made to determine the effect of different durations of the hot chemical etching and of the anodic etching. It was found possible to get deposits of copper if the anodic etching is omitted if the chemical etching period is lengthened, but the deposits do not stick. The duration of the anodic etching required, depends on the thickness of the subsequent copper deposit; ten seconds are sufficient for a copper deposit of twenty minutes duration in the above cyanide bath, but for a deposit of two hours duration, thirty seconds anodic etching is required. As a result of these experiments the following process for copper plating aluminum is recommended: etching the grease-free surface in 10% NaOH saturated with NaCl until uniform evolution of gas takes plate (½ to 1½ minutes), was with water, dip in 2% HCl solution, wash, anodic etching in normal monochloracetic acid with 20 to 25 amperes per square decimeter (about 200 to 250 amperes a square foot) at 50 to 60 volts when the anode is 2.3 inches from the cathode. This lasts 10 seconds in 2 minutes, according to the duration of the subsequent plating.

After washing, the surface is etched 10 to 20 seconds at 90 to 95 deg. C. (200 dg. F.) in a solution of 23 grams Na_2CO_3 and 45 grams $NaHcO_3$ in a liter, is washed and plated in the cyanide bath with 0.3 ampere per square decimeter from one half hour to several hours. After one half hour the object may be changed to an acid copper sulfate bath in order to save time.

The current efficiency in both cyanide and sulfate baths is not as good in the early stage of deposition as later. In the cyanide bath the mean value for the first twenty minutes is 62%, for the first hour 75%, and for longer periods 80%. In neutral sulfate solution the values are: for 20 minutes 85%, and for one hour 97%. The mean thickness of the deposit after plating in the cyanide bath for 20 minutes is 0.00006 inch, after one hour 0.0002 inch; in the sulfate bath, after 20 minutes 0.0003 inch, and after one hour 0.0005 inch.

This process has the disadvantage that it is complicated and uses a large amount of energy. An attempt was, therefore, made to substitute chemical etching for the electrolutic, as proposed by H. K. Work (Trans. Am. Electroch. Soc. 53, 263 (1928) for nickel plating. This was not found possible.

From experiments on soldering, it was found that a heavy plate is necessary, preferably from a sulfate bath.

E. Smith and C. A. Velarde have an article in Mineral Industry (London) Vol. 38, p. 297, (1931), in which a process of obtaining a highly polished plate on aluminum is described. This consists in etching in potash, treating in a bright dipping bath of nitric and sulfuric acids, plating with nickel, and then heating to 900° F. for 10-15 minutes. It is said this causes the two surfaces to alloy and can be given a high polish and then chromium plated.

A. Kutzelnigg, of Vienna, has an article on plating by dipping and by contact, in the Zeitschrift f. Elektrochemie, Vol. 38, p. 154, (1932.) He says that the process of plating by dipping is used abroad extensively for cheap deposits of gold, silver, copper or tin on brass, or for preparing aluminum for further plating.

The simplest procedure is to deposit the metal from a cold solution, when it is called dip plating. If the plating is in a boiling solution, it is called the boiling process. Often it is convenient to plate by rubbing a paste on the surface; it is then

called the rubbing process. The paste is a solution of a salt of the metal in some absorbent material. If another metal of higher solution pressure furnishes the current, it is called the contact process. Both of these processes are due to the different tendencies different metals to go into solution, which is measured by the potential difference between a metal and a solution of one of its salts. The metal that has the greater tendency to dissolve, always forces one with a less tendency out, depositing the more noble metal on itself and on any other more electropositive in contact with it. The fact that metallic zinc in contact with gold dipping in a zinc sulfate solution deposits zinc on the gold is no exception to this, but it is due to the fact that zinc alloys with gold even when cold, and zinc in this alloy has less tendency to dissolve than pure zinc. In the same way copper is covered with zinc if copper is placed in contact with zinc and boiled in a zinc sulfate solution. Zinc can also be deposited on copper by boiling the copper with ammonium chloride and zinc dust.

The tendency of a metal to dissolve depends on the solution into which it is dipped, that is, it depends on the concentration of its own ions in the solution. For this reason the relative positions of metals in the electrolytic series can be altered. Consequently copper can deposit zinc from concentrated potassium zinc cyanide, though very slowly; two hours were required in a cold solution to show a distinct zinc color. Other examples of the same kind are that copper deposits antimony from sodium, sulfantimonate, and silver deposits arsenic from arsenic chloride solution.

The anion is of influence on the possibility of deposition thus aluminum does not deposit copper from copper nitrate or copper sulfate, but does from the chloride. On iron, copper forms a bright deposit from sulfate but from the chloride in a loose, badly adhering form.

The less active potential difference, the more uniform is the deposit, and if the rate of deposition is very great the metal comes down black or discolored.

Sometimes the deposit contains both metals. Zinc and cadmium are especially apt to form alloys with the metals they deposit. Zinc throws down a black precipitate from silver nitrate containing varying amounts of zinc and silver. From dilute copper sulfate, zinc throws down a black precipitate that when

burnished, gives a yellow metallic appearance. Gold and platinum also form zinc alloys in the same way. On the other hand, lead, tin and cadmium are deposited by zinc in a nearly pure state.

For gold plating by dipping, potassium gold cyanide is most generally used. Another group of solutions contains sodium phosphate or pyrphosphate.

Silver plating by contact is usually carried out in a boiling solution of potassium silver cyanide. The dip process without a contact metal is too slow. A solution of sodium silver thiosulfate at boiling temperature gives brilliant deposits on copper and brass.

Tin plating by dipping can be effected in a boiling potassium cyanide solution.

It is well known from the work of Kohlschütter and his collaborators that electrodepositions frequently contract on standing. This is shown by the deformation of the underlying metal if this is sufficiently flexible. C. Marie and N. Thon have shown, however, in an article in the Comptes Rendus, Vol. 193, p. 31, (1931), that in some cases expansion takes place. The facts observed are as follows: In a neutral solution of 200 grams of hydrated copper sulfate in a liter and a current density of 1.1 amperes per square decimeter, expansion was observed on polished platinum, gold, silver and copper. On platinum with a dull finish contraction was observed. When 1% of sulfuric acid is added to this solution, expansion was observed which in some cases changed into contraction. In solutions containing 2 to 3% sulfuric acid, contraction was observed in all cases.

In a solution containing one gram mole of cuprous chloride and four and one half of sodium chloride and some hydrochloric acid, expansion is always obtained.

Deposits of zinc from the sulfate, chloride and cyanide always gives expansion.

The results show that metal deposits have a tendency to contract or to expand, and this is certainly of importance for the question of adherence of electro deposits.

ELECTROPLATING ZINC ON ALUMINUM

By Harold K. Work
Aluminum Company of America
Read at the Philadelphia Convention, 1932

As a result of the recent investigations of Dr. Cocks in England, the plating of zinc on aluminum has received considerable attention. The work which has already been done by others will be reviewed briefly in this paper, and the results of some work carried out in the Aluminum Research Laboratories will be reported.

Earlier Investigations

At various times publications on the zinc plating of aluminum have appeared. It was not until recently, however, that it was recognized that zinc, in spite of its relative position in the electromotive series, would electrochemically protect aluminum. Seligman and Williams[1] pointed this out in 1920, but concluded at that time that such protection was not practical.

Sutton and Sidery[2] investigated the question in a broad study of the protection of aluminum against corrosion. They found that electrodeposited coatings of zinc, 0.0005″ thick, afforded better protection to aluminum than did coatings of cadmium of similar thickness, but that the two types of deposit appeared to give an approximately equal degree of protection when applied to alloys of aluminum. They sand-blasted the aluminum surface prior to electroplating to secure adhesion of the electroplate. Cyanide baths of low free cyanide content and a sulfate bath containing betanaphthol as an addition agent, were found to be satisfactory. The corrosion tests which they used consisted of sea-water "wet and dry" tests and sea-water spray tests. On the better samples good protection was noted at twelve months, but at twenty months pitting was observed.

Shortly after the above publication the author[3] stated briefly that aluminum could be electroplated on from a cyanide solution and that other metals could then be electroplated over the zinc. Except where zinc alone was the coating metal, however, the corrosion resistance of the electroplate, unless heat-treated, was poor. Before plating, the aluminum surface was not given any special preparation to roughen the surface, but was

[1] J. Inst. Metals 23, 172 (1920)
[2] J. Inst. Metals 38, (No. 2), 241 (1927)
[3] Trans. Am. Electrochem. Soc. 53, 361 (1928)

merely cleaned by a brief immersion in a hot, mildly alkaline solution and dipped for 60 seconds in 5% hydrofluoric acid.

After experimenting in a general way with electroplating directly on an unroughened aluminum surface from numerous cyanide solutions, certain generalizations were derived concerning the best type of solution to use. Such a solution should be characterized by (1) a metal high in the electromotive series, (2) a minimum tendency to attack aluminum, (3) an addition agent, (4) a minimum gas evolution at cathode.

A solution answering these requirements is the following:

	g./L.	*oz./gal.*
Zinc cyanide, $Zn(CN)_2$	30	4
Sodium cyanide, NaCN	30	4
Ammonium hydroxide, NH_4OH (Sp. G. 0.90)	30	4
Peptone or	1	0.12
Gelatin	5	0.67

Solution used at room temperature

Of various solutions tested, those having zinc (a metal high in the electromotive series) consistently gave the best results. Other solutions tended to give blistered deposits. Even in plating with zinc it was necessary to modify the usual type of highly alkaline solution. Such solutions attacked the aluminum and only by exercising special care could the electroplates be applied directly. Substitution of ammonium hydroxide for sodium hydroxide reduced this difficulty, but did not completely eliminate it. An addition agent was needed for best results. Of various addition agents tested, peptone, gelatin, and gum arabic were most satisfactory. Peptone was most effective, but when a bath was used intermittently, gelatin gave more constant results. For continuous plant use peptone has given better service. In using this solution the free cyanide content should be maintained as low as possible, although a small amount is advisable to prevent coating of the anode.

In order to avoid blistering it is better to operate at low current densities, 0.5 amp./sq.dm. (5 amp./sq.ft.) or less. Plates applied from the above solution adhere well to the aluminum. As a preparation for such plating the aluminum merely has to be cleaned in a mildly alkaline cleaner of 7.5 g./l. (1 oz./gal.) each of sodium carbonate and trisodium phosphate and given a one-minute dip in 5% hydrofluoric acid. This does not specially roughen the surface. Due to the low current density used in the plating, this particular cyanide solution finds its greatest ap-

plication in the formation of a thin preliminary coat before other more rapid plating solutions are applied. A variety of electroplates have been applied over this thin zinc electroplate and very adherent deposits have been obtained. Unfortunately, however, with the exception of zinc and special heat-treated combinations, these secondary coatings are not particularly resistant to corrosion. The softer metals, such as copper, usually blister on exposure to moisture or in the salt spray test, while harder metals, such as nickel, usually peel. On the other hand, where zinc alone is the coating metal this type of corrosion does not take place. In fact, the aluminum is actually protected by the zinc.

The method of zinc plating used for the corrosion experiments reported later, consisted in applying a five-minute electroplate of cyanide zinc from the above solution and then plating thirty minutes in the following acid bath[4] at 3 amp./sq.dm. (28 amp./sq.ft.) to give a deposit 0.025 m.m. (0.001 in.) thick:

	g./L.	*oz./gal.*
Zinc sulfate, $ZnSO_4.7H_2O$	360	48
Ammonium chloride, NH_4Cl	30	4
Sodium acetate, $NaC_2H_3O_2.3H_2O$	15	2
Glucose	120	16

While a cyanide bath could be used for the latter coating, this acid bath is somewhat easier to operate. Other acid baths will also give good deposits.

As has been indicated earlier, judging from the relative position of the metal in the electromotive series alone, it would not be expected that zinc would electrochemically protect aluminum from corrosion. That this is actually the case, at least under certain conditions, has already been indicated. Potential measurements of metal couples by Edwards and Taylor[5] have shown that in normal sodium chloride solutions zinc is electronegative (anodic) to aluminum. Such behavior of two metals is not uncommon, and is usually a result of passivity induced by a surface film on at least one of the metals.

Dornauf[6] compared cadmium and zinc electroplates for the protection of aluminum. His corrosion tests of 50 days, using 3% sodium chloride solution, favored cadmium.

H. C. Cocks[7] extended the work of Sutton and Sidery on zinc plating on aluminum. He made a broad study of plating solu-

[4] Blum & Hogaboom, Electroplating & Electroforming, p. 324, (1930)
[5] Trans. Am. Electrochem. Soc. 56, 27 (1929)
[6] Korrosion u. Metallschutz 4, 97-102 (1928)
[7] Journ. Electroplaters' & Depositors' Tech. Soc. 5, 83 (1930)

tions and as a result of this study preferred sulfate baths for deposition on aluminum alloys except in the case of irregularly shaped articles. Gum arabic was considered the best "addition agent" for the solution. He applied the zinc to a sand-blasted aluminum surface. His electroplates, which were one-half as thick as those reported on later in this paper, resisted a sea salt water spray (a few minutes three times a day) for about a year. He considered these results quite satisfactory.

Akimov[8] demonstrated that zinc protects duraluminum in Black Sea Water even to quite a distance from the area actually covered by zinc. He advances an electrochemical theory based on the formation of a surface film on the aluminum to explain this.

Corrosion Tests[9]

In order to determine quantitatively the corrosion resistance of zinc plated aluminum, samples were plated by the procedure outlined as that preferred by the author. That consisted of applying a thin plate from a cyanide bath to an unroughened surface and then finishing the plating in an acid bath.

The corrosion tests[10] used in this investigation, consisted in measuring the change in physical properties of the plated and unplated aluminum, resulting from exposure to a 20% salt spray. With 17 ST (Cu 4.0; Mn 0.5; Mg 0.5) corrosion was temporarily prevented by plating with zinc. At the end of four weeks in the 20% salt spray the zinc-plated specimens showed no loss in physical properties, while with the unplated metal a noticeable loss had occurred. At the end of twelve weeks this loss had increased and a small loss had also appeared for the zinc-plated metal. This would indicate that the zinc had protected the aluminum for fully four weeks, but dissolved after that period and lost its protecting property. Such protection is quite good and undoubtedly has value for certain applications. For general use, however, a duplex aluminum product developed by E. H. Dix, Jr., of the Aluminum Company of America, has greater value. This is known as "Alclad"[11] 17ST, and consists of an aluminum alloy core covered by a surface layer of pure aluminum, which is alloyed and integral with the core. Under similar conditions to those used for testing the corrosion of the zinc-plated

[8] Z. Metallkunde 23, 249 (1931)
[9] Trans. Electrochem. Soc. 60, 117 (1930)
[10] Supplied by courtesy of Dr. L. J. Weber, Aluminum Co. of America
[11] Dix., E. H., Nat. Advisory Comm. for Aeronautics, Technical Note 259, Aug., 1927.

17ST, "Alclad" 17ST has maintained its physical properties for several years. When zinc-plated 2S (commercially pure aluminum) was tested similarly for corrosion resistance, the electroplated metal lost in physical properties more rapidly than the unplated metal until the zinc was dissolved. This no doubt indicates that the zinc in protecting the aluminum dissolves more rapidly than the aluminum itself and has little value in protecting 2S under the above conditions.

Applications

The commercialization of zinc plated aluminum in this country has been restricted to a few special uses. Zinc has been electroplated on the lower edge of several hundred thousand radio shield cans to secure a special type of contact between the can and its support. Manufacturers of rubber goods have zinc plated aluminum to meet requirements that aluminum alone would not satisfy. In a few instances, where "Alclad" metal could not be used, zinc electroplating has been substituted to advantage, to resist corrosion. Electroplates of zinc have been put on aluminum commercially to prevent the seizing of threaded parts.

Zinc-plated aluminum also has an interesting property that ought to be of value. It may be soldered by ordinary procedures, providing the electroplate is at least 0.008 m.m. (0.0003″) thick and that the electroplating has been properly applied. If the coating is thinner the zinc apparently dissolves in the solder, and the ordinary procedures can not be used.

Summary

Electroplates of zinc electrochemically protect aluminum from corrosion. Although this protection is not as permanent as may be obtained by other means it is proving valuable commercially for certain special applications. Zinc electroplates have also been of value where properties of the zinc other than corrosion resistance are desired on an aluminum surface.

DEVELOPMENTS IN METAL LACQUERS

L. M. Hayden
Stanley Chemical Company
Read at the Philadelphia Convention, 1932

The subject of keeping plated finishes in their original appearance without change of color, brightness and luster is one which I feel is of vital interest to you all.

Certain plated finishes, such as chromium plate, retain all their original appearance without a protective coating. The majority require a clear transparent coating to keep them free from tarnishing and other surface changes.

This subject is one about which you hear all the time and yet you are never free from trouble and one more viewpoint may bring to you suggestions or help which will enable you to produce better, lasting plated finishes.

You, of course, are all familiar with the work of W. T. Barrows, of the Bureau of Standards, who with the fund supplied by your organization, made such a fine study of "The Spotting of Plated or Finished Metal". I will take the liberty to quote this work quite frequently as a great deal of the basis of the work which our laboratory has done was founded upon it.

There are a great number of factors which contribute to the discoloration or disfigurement of metal finishes, whether they may be made from a solid metal such as an article manufactured from a piece of strip brass, or whether it be a plated article manufactured from a piece of cold rolled steel, brass plated.

The types of discoloration or disfigurement which give the most trouble in actual manufacturing are the ones which are supposed to be taken care of by a Clear Metal coating. These are as follows:

1. Tarnishing or discoloration of the finish
2. Crystal Spotting
3. Stain Spotting

We will take each of these disfigurements of manufactured articles individually, with care, so that we may thoroughly understand what causes each and how they may be remedied.

1. Tarnishing or discoloration of the finish.

This division might again be subdivided into four further subdivisions, namely;

(*a*) Tarnishing of the metal due to poor cleaning prior to application of the clear protective coating.

(*b*) Tarnishing of the metal due to the handling of a properly cleaned article, with dirty or greasy hands or gloves.

(*c*) Tarnishing of the metal by the reaction of the lacquer film while drying, with the surface of the metal.

(*d*) Tarnishing, due to the effect of sulphur or hydrogen sulphide on finishes other than those which contain copper sulphide, silver sulphide or nickel sulphide.

Now let us take each of these subdivisions and see what its cause and remedy may be.

(*a*) Tarnishing of the metal due to poor cleaning prior to application of the clear protective coating. The proper cleaning of plated articles, you are far more familiar with than I am, but I would like to stress the point, that the proper adhesion of a clear protective coating as well as possibility of discoloration is directly proportional to the cleanliness of the article prior to the application of this clear protective coating.

(*b*) Tarnishing of the metal due to the handling of a properly cleaned article, with dirty or greasy gloves or hands. I'll pass over this part rapidly, merely stating that I have seen plated articles which apparently were fine when they were finished with this clear protective coating, but after standing for a while showed up a distinct thumb mark which was underneath the lacquer. This came from somebody's handling the polished surface after it had been cleaned and prior to the application of the clear protective coating, and the oil and acid present on the hand of the operator, eventually caused a discoloration of the finished surface, even though the lacquer had been applied.

(*c*) Tarnishing of the metal by the reaction of the lacquer film while drying with the surface of the metal. This type of discoloration is more unusual than the first and second which we have just discussed and occurs practically only in very humid, damp weather. If you take a lacquer which contains resins whether they be synthetic or natural, having a fairly high acid content and use a thinner or a retarder in damp, humid weather to stop blushing, you may experience a discoloration of the finish where, let us say, a highly polished, bright brass finish will turn into a finish which looks partly oxidized. This is caused by improperly designed lacquer thinners. If the proper thinner is used, or proper retarder, there will be no discoloration of this nature.

(*d*) Tarnishing due to the effect of sulphur or hydrogen sulphides on finishes other than those which contain copper sulphide, silver sulphide, or nickel sulphide. Probably of all the discolorations of metal finishes this is the most common and also in mild form, is the least noticeable. When

a certain article such as silver has a slight tarnish caused by sulphur or hydrogen sulphide, it shows up very readily in the dulling of the finish. In the case of brass it may merely show a slight darkening of the finish unless the tarnish is pronounced. The cause of this type of discoloration comes:

1. From the air.
2. From the use of wrapping paper containing sulphur or sulphide, such as kraft paper or cardboard boxes.
3. Rubber—in this case the most common place where it occurs is electric light fixtures where they are already wired.

In order to prevent this type of tarnishing there are three things which should be carefully looked into.

1. The paper and boxes which come directly in contact with the article should be as free from sulphur as possible.
2. In the case of rubber, non-blooming rubber should be used wherever possible.
3. Lacquer should be employed which resists this type of tarnishing. It has been found, that certain types of resin incorporated in the lacquer, produce films which resist this sulphur to a very marked degree. Where this type of tarnishing is encountered on silver work a silver lacquer designed primarily for this purpose should be employed.

It is a strange thing but a great many people have confused the test for this tarnishing of metal with the test for crystal spotting. The reason for this is quite natural I suppose, due to the fact that sulphur in both cases causes in one case, the tarnishing, and in another case, the crystal spotting. However, crystal spotting occurs only on finishes containing copper sulphide, silver sulphide or nickel sulphide in the actual finish.

The best test for tarnishing is to carry out the following procedure.

Take some pieces of pure silver say 2″ x 2″ and approximately $\frac{1}{16}$″ thick, clean them thoroughly and apply your lacquer and allow the lacquer to air dry for approximately a half hour and then bake it for thirty minutes at approximately 150° F. The plates should then be aged in the air for approximately twenty-four hours. This is necessary, due to the fact that in the case of certain types of synthetic resins which do not dry entirely by the evaporation of solvents, but dry through oxidation, those lac-

quers should not be tested until they have had a chance to age properly.

The panels coated with the various lacquers, should be exposed to an atmosphere of hydrogen sulphide, under a slight pressure, in a bottle. After thirty minutes they should be examined and this examination should be repeated from time to time and each time the panels are removed they should be rated in accordance with the amount of discoloration. This type of test will show conclusively those lacquers which withstand the action of sulphur or hydrogen sulphide in tarnishing silver or brass work.

Instead of using silver you can use soft rolled copper, but the tarnish on the silver is very much more readily determined in the early stages than it is on copper.

Although the tarnishing of finishes and crystal spotting are caused at least in part by the same thing; namely, sulphur or hydrogen sulphide; nevertheless over a period of years and hundreds of tests, we have found that the best lacquer to withstand tarnishing is not the best lacquer to withstand crystal spotting. Apparently, there is some factor which we have not been able to determine which differs in these two failures of plated surfaces.

Now that we have covered fairly completely the tarnishing of discoloration of the finish, let us go to the second type of failure, namely "Crystal Spotting".

2. Crystal Spotting. Just how this formation occurs is not definitely known but the formation of these crystals are accelerated by sulphur either as free sulphur or hydrogen sulphide. How this sulphur is introduced into the atmosphere seems to make no difference, as it may come directly from the atmosphere or from rubber or from paper which is directly in contact or near the sulphide finish.

Crystal spotting does not appear on sulphide finishes which are not lacquered or which do not have a protective coating.

Warm weather or an increase in temperature increases the growth of crystal spots when sulphur is present, but high humidity does not increase them.

The best remedies for stopping this crystal spotting are as follows:

1. The exclusion of sulphur from the surroundings.
2. The use of wax paper for wrapping.
3. The use of a lacquer which will retard or stop this spotting.

Let us go back to Barrows' work on this subject, and you will remember that the composition of the base metal underlying the coating of copper or brass has no influence on the growth of crystal spots, nor does the previous treatment of metals with acids or alkalies, affect the growth of the crystal spotting.

Therefore, the above three methods of reducing this type of spotting are all that is necessary to produce finishes practically free from this defect.

1. The exclusion of sulphur from the surroundings. This merely means that you should use in boxes, which your articles are packed in, cardboard as free as possible from sulphur or sulphur containing salts and the wrapping paper which your articles are directly wrapped in should be free from sulphur.
2. The use of wax paper for wrapping. It was found that by this method there was a distinct decrease in crystal spotting.
3. The use of a lacquer which will retard or stop this spotting. Through a considerable amount of research work and innumerable tests on sulphide finishes, it has been found that certain types of nitrocellulose lacquers have a distinct resistance to the penetration of volatile sulphur compounds. Therefore, if you use a lacquer which has these characteristics you will reduce this trouble practically entirely.

As you know, the growth of crystal spots may not occur for a considerable length of time after the article is finished. Therefore, a quick test should be employed and the one which has proved by far the most satisfactory is as follows:

Take some copper plated strips and treat them to produce the "copper oxide finish" and buff the copper oxide finish through to the copper plate in spots, so that you will have on the panel, parts which are black oxidized surfaces and parts which are bright copper surfaces. Clean thoroughly and apply a lacquer coating. After this lacquer coating has thoroughly dried and by that I mean a matter of seventy-two hours or more, place these test pieces in a desicator. On the top of each piece, put a piece of laboratory filter paper next to the oxidized and lacquered surface and then sprinkle on top of the filter paper a thin film of flowers of sulphur.

Close the desicator and allow the pieces to remain in there for twenty-four hours. At the end of the twenty-four hours, examine the pieces by removing from test panel the filter paper

sprinkled with the sulphur. Repeat this examination every twenty-four hours until a definite conclusion is reached. You will find that certain lacquers will withstand this treatment practically perfectly, showing no signs of black crystal spots either on the polished surface or on the copper oxidized surface. Other lacquers will show very prompt failure.

After determining the type of lacquer which meets this requirement, do not forget that an increase in the thickness of the lacquer coating retards the growth of crystal spots. That does not mean that it is necessary to apply two coats, but if you are spraying and the lacquer can be thinned satisfactorily, one part of lacquer to one part of thinner, or could be thinned, two parts of lacquer to one part of thinner and still apply properly it is better to use the mixture of two parts of lacquer and the one part of thinner as you will apply a thicker residual coating on your article with the smaller amount of thinning.

As you know, we are associated with the Stanley Works of New Britain who are large manufacturers of hardware and tools. A great number of the finishes on their hardware are plated. Through exhaustive tests in conjunction with their laboratory in actual large scale manufacturing operations and over a period of a good many years we have found that the above test compares excellently with actual results. In other words, a lacquer which withstands the flower of sulphur test will stand up in manufacturing operations excellently and show practically no crystal spotting.

Just as an example of what the effect of sulphur in paper or cardboard may mean in packing your finished articles, we recall instances of a number of years ago when the subject was not thoroughly understood where hinges with an oxidized finish, were examined after being in storage for six or eight months. They were found to have crystal spotting on the outside leaves of the hinges as removed from the box. By that I mean the leaf facing the bottom of the box and the leaf facing the top of the box showed crystal spotting, while none of the hinges in between showed any whatsoever. In other words, the two parts which were nearest to the cardboard box (and the cardboard box did contain sulphur compounds) had crystal spots on the oxidized surfaces, while those parts which were not next the cardboard and more protected did not show any spotting whatsoever.

As you know, one of the worst features of crystal spotting is

that the spots do not appear rapidly and for this reason it is extremely difficult for the manufacturer to make sure that his articles will not show this type of spotting. Often times he will not know that he is getting, or let us say is going to get, this type of failure until he gets complaints from his customers. For this reason, he should take every care to prevent this type of failure.

3. Stain spotting. Stain spots as you know, appear on both lacquered and unlacquered specimens whether they be oxidized or unoxidized and they can also appear on plated and unplated articles.

There are three factors which are usually present in causing stain spots:

1. The first of these is the porosity of the metal or the plating.
2. The presence of moisture absorbing compounds which are held in these pores.
3. The absorption of moisture by these very compounds in the pores. This absorption causes the absorbed salts to creep out over the surface causing stains and in extreme cases actual crystallization of solid material on the surface of the finished article.

Articles whether they be lacquered or unlacquered when exposed to humid conditions will show up stain spotting within a few hours or at the most, in a few days, except where the finishing material whether it be a nitrocellulose lacquer or not, has the quality of good impermeability to water vapors and resistance to the chemical compounds which have remained in the pores of the metal.

So far no laboratory test has been found satisfactory for determining the resistance of lacquered articles to stain spotting. There have been a number suggested and tried out carefully, in comparison with actual manufacturing results, but none of them have been found to be anywhere near accurate.

The best method of testing which we, with the assistance of The Stanley Works laboratory, have found, has been to actually run plant tests on malleable iron castings which were brass plated and scratch brushed. If you take a sufficient number of such articles and after lacquering and thoroughly drying of the lacquer, expose them to moist atmosphere let us say right in the plating room; within twenty-four to forty-eight hours you can

come to a definite conclusion as to the value of any lacquer as a protective coating to withstand stain spotting.

We have run hundreds of tests in actual plant work and run all kinds of checks from time to time and invariably if you do a sufficient number of pieces, let us say a hundred, with each lacquer, definite conclusions can be reached.

The three best methods of reducing stain spotting are as follows:

1. See that your castings are as free from porosity as possible. In some cases this may be difficult but we have found a great many instances where better foundry practice will help greatly.
2. You can reduce stain spotting by the elimination of alkaline cleaning or plating solutions and help by good cleaning, although in a great many cases, unfortunately, this expedient can not be actually done in plant operation.
3. A nitrocellulose or synthetic resin type of lacquer designed particularly for reducing this stain spotting should be used and where it is used the minimum amount of stain spotting will occur.

As far as we know, no clear protective coating has been produced that will give you 100% results throughout. By that I mean, that one lacquer will not give you perfect protection against sulphur stain, crystal spotting, stain spotting and protection to outdoor exposure. We have examined hundreds of clear protective coatings. Some gave excellent protection to certain failures—let us say crystal spotting, but on the other hand were complete failures on stain spotting. We have examined lacquer that was outstanding in so far as outdoor exposure was concerned but were complete failures to both types of spotting. We have seen extremely few that would stand outdoor exposure, sulphur stain and tend to reduce both crystal and retain spotting. There are some that are good on outdoor exposure, sulphur stain and will tend to reduce either stain or crystal spotting, but not both. Therefore, if you use care in selecting the lacquer for your particular problem you will without question reduce your finishing troubles to a minimum.

ON THE ANODIC DEPOSITION OF RUBBER

By Albert Hirsch
Philadelphia Branch
Read at the Philadelphia Convention, 1932

This experiment was carried out to demonstrate that a plater can and does profit by the results of research. Therefore, the procedure is given in some detail. From a survey of the literature it was learned that nearly everything in connection with the subject is patented in one form or another. Likewise the anodic deposition of rubber is also a patented process.

Latex is the name given to the liquid from the rubber trees, which on coagulation yields about 33% rubber. The latex is treated in various ways to prevent coagulation and sold under different trade names according to the process used to stave off coagulation. For instance, Lotol is a form of latex treated with about 4% ammonium hydroxide to prevent coagulation. Vultex is vulcanized latex and is also a patented process. Revertex is a highly concentrated latex, produced by evaporation. It contains about 80% rubber.

Principle of Rubber Deposition.

Reuss*, while electrolyzing a water solution with a clay diaphragm, observed that while the water was being forced by the current through the diaphragm toward the cathode, the solid particles moved toward the anode. The former process is electrical endosmosis and the latter electrophoresis. Therefore, in this case, if a colloid is formed with the lotol, sulphur pigments, softeners, accelerators, etc., the particles will deposit in combination with the rubber upon a zinc anode in the same proportion as they are in the mix. When a suspension of this kind is electrolyzed there is a creaming around the anode and layers of rubber are built up.

Rubber is an insulating material; then, how is it deposited? Dr. Sheppard[2] pointed out that if the anode is coated with gelatin or a fabric, layers of rubber will deposit upon it. He likened the creaming of the latex on the bare anode to deposition on the fabric and gelatin, where the current from the anode passes through the pores and causes deposition.

Procedure.

When compounding rubber or the mix, as it is sometimes called, the proportions are usually based upon one hundred parts

*Wiedmann, Elektricitat, 1, 1007, (1893)
[2] Trans. Am. Electrochem. Soc. 52, (1927)

of rubber. In the following formula the proportions are rounded off for one liter of lotol, which contains about 37% rubber.

Formula:—

Suspension A	*Approximate g/L of Lotol*
Zimate	3.75
Agerite	3.75
Zinc oxide	9.37
Sulphur	8.44
Carbon black	3.75
Casein (dissolved in 30% solution of sodium hydroxide)	7.5
Hot water	32.8

Soap Solution	*g/L of Lotol*
Oleic acid	8.2
Ammonium hydroxide (conc)	18.75
Hot water	24

Note: Suspension A is prepared by grinding the powders very finely in a mortar. It is then necessary to wet the powders. This can be done with casein dissolved in a 30% solution of sodium hydroxide. The casein-sodium hydroxide solution is usually left standing over night, before it is used.

Suspension B.

The soap solution as prepared is stirred into the lotol and forms what is known as Suspension B. Suspension A is stirred into Suspension B and the mixture is ready for use. If a colloid mill is available, it would not be necessary to grind the powders in the mortar. "Zimate" is a zinc salt of dimethyldithiocarbamic acid, an ultra accelerator. "Agerite" is a trade name of a strong anti-oxidant. It is an aldehyde amine condensation product. These compounds can be purchased from the Vanderbuilt Company, New York.

Apparatus.

A glass battery jar 9″ x 6.5″ x 8″ deep; one "B" battery, 22.5—45 volts; resistance coil, ammeter, lead cathode, zinc anode and a drying oven of laboratory size were used.

Thin deposits were obtained in about 10 minutes with a C. D. of 1.5 amperes / dm^2 or about 14 amperes/sq. ft. at 45 volts. The deposits were dried a few minutes in the oven at about 210 degrees F. and finally dipped in talc powder. Heavy layers of rubber can be obtained from vultex or revertex in the same length of time. In comparing rubber deposition with a metal

like nickel, it has been found that 68 times as much rubber will be deposited as nickel with the same current density and time.

See U. S. Patent No. 1,476,374, Sheppard & Eberlin, British Patent No. 223,189, Klein & Szegvari.

(Mr. Hirsch followed the paper with a demonstration of plating rubber according to the methods outlined.)

THE ELECTRODEPOSITION OF TUNGSTEN FROM AQUEOUS ALKALINE SOLUTIONS

M. Leslie Holt and Louis Kahlenberg

It is quite commonly recognized that a satisfactory coating of electroplated tungsten would be specially valuable as a protection for base metals as well as for ornamental purposes. Tungsten is resistant to ordinary acids and other chemical reagents. For example, it is not attacked by hydrochloric or sulphuric acid, as is chromium. A mixture of nitric and hydrofluoric acids will dissolve tungsten, but these reagents would hardly ever come in contact with an electroplated article in ordinary use.

I. HISTORICAL INTRODUCTION

Many attempts to electrodeposit tungsten on various metal surfaces are recorded in the literature. These may be divided into three classes according to the type of plating bath used-namely—(1) fused or molten bath, (2) non-aqueous bath and (3) aqueous bath. The records of these numerous attempts show a variety of electro-reduction products such as the blue oxide W_2O_5, the brown oxide WO_2, the black oxide WO, the finely divided black metal, the silvery metal and the tungsten bronzes. The so-called bronzes are really combinations of the oxides, or various proportions of alkali oxide and tungsten oxides which give the purple, green and blue products.

1. *Deposition from fused Baths*

Schiebler (J. prakt. Chem. 83, 322—1861) obtained only tungsten bronze upon electrolysis of various fused tungstates. Zettnow (Pogg. Ann. 130, 16—1867) used a bath of molten sodium tungstate and obtained a black powder which he said was metallic tungsten. Hallopeau (Compt. rend. 127, 755—1898) electrolized fused lithium para-tungstate and noticed crystals of tungsten at the cathode. Stavenhagen (Ber. 32, 3064—1899), however, obtained only a lithium tungsten bronze

from the same bath. Knorre (J. prakt. Chem. N. F. 27, 58—1883) also obtained tungsten bronze deposits from molten tungstates. Martin (Z. anorg. Chemie 65, 311—1910) obtained a deposit of tungsten from a bath of moltey cryolite in which was dissolved some tungstic acid. Van Liempt (Z. anorg. Chem. 122, 175—1922; Z. anorg. Chem. 143, 285—1925; Z. Elektrom. 31, 249—1925) used baths of fused lithium and sodium tungstates in which tungstic acid was dissolved and obtained deposits of tungsten as well as some tungsten bronzes. Mann and Halvorsen (Trans. Am. Electrochem. Soc. 45, 13—1924) used a bath of fused lithium chloride with a tungsten anode and secured cathode deposits containing tungsten. Kahlenberg (Trans. Am. Electrochem. Soc. 46, 181—1924) used a fused bath of sodium and potassium chlorides in which tungstic acid was dissolved and obtained, under certain conditions, good deposits of tungsten. However, these deposits were quite thin. L. Andrieux (Ann. Chim. (10) 12, 423—1929) deposited metallic tungsten by electrolysis of tungstic acid dissolved in fused alkali borates and fluorides. Hartmann (Ebert & Bretschneider Z. Anorg. Chem. 198, 116—1931) used baths of fused alkali phosphates and tungstic acid and deposited both alpha and beta tungsten in metallic form as shown by Röntgenographic studies.

2. *Deposition from non-aqueous Baths*

Rosenheim (Z. angew Chem. 22, 1153—1909) electrolized a solution of tungstic acid in alcohol saturated with hydrochloric acid gas and obtained only a lower valence tungsten salt. A German patent (German patent No. 231,657—1910) describes the deposit of tungsten from pertungstic acid in various solvents. Fischer (Z. anorg. Chem. 81, 170—1913; Z. anorg. Chem. 81, 102—1913) failed in his attempts to electrodeposit tungsten by the method described in this patent. Another German patent (German Patent No. 237,014—1920) describes the deposition of tungsten from solutions of tungsten salts in such solvents as acetone. Fink (Trans. Electrochem. Soc. 59, 461—1931) failed to get results from the mentioned solutions in this patent and also from those of the earlier patent. Neumann and Richter (Z. Elektrochem. 30, 474—1924) tried electrolysis of tungsten hexachloride in acetone, pyridine and glycerine respectively with no results. Mann and Halvorsen (loc. cit.) also attempted to electrodeposit tungsten from solutions of the hexachloride

in organic solvents. McKee and Mann (McKee, Mann & Montillon, Trans. Am. Electrochem. Soc. 53, 533—1928) used ammonium iodide in furfural as the electrolyte with a tungsten anode and a copper cathode with no result. L. St. C. Broughall (British patent 320818—1928) electrolyzed a solution of a tungsten salt in liquid ammonia at a low temperature or a high pressure. Booth and Merlub-Sobel (J. Phys. Chem. 35, 3303—1931) failed to deposit tungsten from a solution of tungsten pentabromide in liquid ammonia. They also tried potassium iodide as an addition reagent for the above solution.

3. *Deposition from Aqueous Baths*

M. Junot (L'Inst. 97—1853—Mellor Vol. XI. p. 692) reduced tungsten electrolytically from a solution of a tungstate in potassium cyanide and alkali hydroxide. Smith (Ber. 13, 753—1880) made the observation that the electrolysis of a neutral solution of a tungstate yields no result, while the acid solution soon becomes blue. Frere (Bull. Soc. Chim. 19, 213—1898) obtained a tungsten amalgam by electrolysis of a hydrofluoric acid solution of tungstic oxide using a mercury cathode. Schaefer (Z. anorg. Chem. 38, 175—1904) electrolized aqueous solutions of sodium tungstate, potassium tungstate and ammonium tungstate and described the various tungsten bronzes obtained. Lieser (Z. Elektrochem. 13, 690—1907) used an acid solution of sodium tungstate with a nickel anode and a platinum cathode and obtained a blue solution containing W_4O_{11}. With a lead cathode he got the brown WO_2. Neither Fischer nor Fink (loc. cit.) could obtain tungsten from aqueous pertungstic acid solutions as claimed in a German patent (German patent—loc. cit. 1910). Reck (Thesis—see Mann & Halvorsen, loc. cit.) tried electrolysis of aqueous acid solutions of ammonium tungstate and sodium tungstate and also a solution of tungsten sulfide with no results. Pearson and Craig (Canadian patent 221041—1922) patented a method for deposition of tungsten from a cell with pasty tungstic oxide in the cathode chamber and sulphuric acid as the electrolyte. Neumann and Richter (loc. cit.) electrolized aqueous double oxalates and double cyanides of tungsten and obtained only the lower oxides. Collenberg and Nillson (Z. Elektrochem. 31, 555—1925) obtained pentavalent tungsten upon electrolysis of an oxalic acid solution of potassium tungstate. Jackson, Russell and Merrill (J. Chem. Soc.

2394—1929) formed a tungsten amalgam by electrolysis of tungstic oxide in 4.6 N-HF solution using a mercury cathode. Fink and Jones (Trans. Electrochem. Soc. 59, 461—1931) succeeded in depositing tungsten from hot alkaline solutions of the tungstates, a bath made by dissolving tungstic acid in saturated sodium carbonate solution being the best. Deposits so obtained on brass or copper cathodes were described as "silvery white" metal but very thin.

II. EXPERIMENTAL

1. *Preliminary Work*

The present investigation was confined to aqueous solutions entirely. We first tried various acid, neutral and slightly alkaline solutions—always with negative results insofar as electrolytic reductions to the metal was concerned. In acid baths the cathode solution became blue, in alkaline it was brown or blue and in neutral solutions there was no particular change in color. The cathode itself was usually coated with a purple or green bronze. In general, the resistance of the various solutions was high so that there was very little current flow. In this preliminary work interest was centered largely on phosphoric acid solutions and slightly alkaline phosphate solutions, for upon addition of phosphoric acid to a sodium tungstate solution, tungstic acid does not precipitate out as is ordinarily the case when a mineral acid is added to a solution of an alkali tungstate. Various concentrations of boric acid, hydrofluoric acid and arsenic acid were also tried. However, the failure to obtain satisfactory results from these solutions, and the success with which Fink and Jones (loc. cit.) electrodeposited tungsten, led us to a further study of deposition from hot aqueous alkaline solutions.

2. *Method and Procedure*

In all of the experiments the following method was used: Pyrex beakers, 100 c.c. size, served as the electrolytic cells. Two of these connected in series were put on a hot plate to keep the solutions at the proper temperature. Each cell was supplied with two 3 cm. by cm. smooth platinum anodes and one cathode of the same size (usually of brass) all supported on an arrangement of ⅛ inch brass rods serving as bus bars. These rods were clamped—insulated—to two glass rod ring stands. Each electrode was cut to leave a narrow 7 cm. "tail", on the end of which

was bent a loop for clamping to the bus bar. When in use each cell was covered with two half circle glass plates to minimize spattering and loss by evaporation. Direct current was supplied to the cells through a switch-board having the usual voltmeter, ammeter and variable resistance. All solutions were made up, heated to the boiling point, and then put in the "beaker cells" on the hot plate. All cathodes used were buffed, washed and then dried with clean filter paper. All switches were closed before the cathodes were put into the cells (two cells were always used together in series). When the "run" was completed the cathodes were taken out before the switches were opened and quickly washed free of the electrolyte.

3. *Various Alkaline Solutions*

The first step was to check our method and procedure by using the baths and conditions suggested by Fink and Jones. The bath contained,

NaOH	70 grams per liter
WO_3	30 " " "
Dextrose	60 " " "

It was electrolized for 15 minutes at about 90°C with a current density of 10 amperes per sq. dm. The brass cathode (weighed before and after deposition) showed a gain of about 0.0015 gram per sq. dm. of surface—the total area of the 3 cm. by 3 cm. cathode being 0.18 sq. dm. However a bath made up of

NaOH	60 grams per liter
Na_2WO_4	38 " " "
Dextrose	60 " " "

and electrolized under the same conditions gave little if any indication of a deposit of tungsten on the brass cathode. The carbonate bath of Fink and Jones was undoubtedly the most satisfactory and this was accordingly the next one tried. The bath as made up contained

Na_2CO_3	330 grams per liter
WO_3	100 " " "

It was electrolized at 100°C for 15 minutes with a current density of 21.6 amperes per sq. dm. This gave a nice silvery tungsten coat on the brass cathode with a gain in weight of 0.019 grams per sq. dm. This deposit clearly weighed much less than 0.078 gram per sq. dm., the amount reported under the same conditions by Fink and Jones. The same bath used 24

hours later under the same conditions gave a deposit of 0.0155 gram per sq. dm. Other carbonate baths of varying composition were also tried with no better results—that is, no thicker deposits.

A series of alkaline baths were tried next with results as indicated in Table 1.

TABLE I.

Alkaline Baths

Time 20 min. Temp. 90°C. Current 8.8 amps. per sq. dm.

Alkaline Agent	*Grams per liter*	*Wo_3 grams per liter*	*Cathode appearance after electrolysis*
NaOH	100	50	Nice shiny deposit
Na_3AlO_3	conc.	50	Fairly nice deposit
$Na_2Al_2O_4$	200	20	No deposit
Na_2AnO_2	conc.	50	Thick dull gray deposit (mostly Zn.)
Na-oleate	conc.	20	No result—too much foam
$Na_3PO_4.12H_2O$	300	100	Nice shiny deposit
Na-benzoate	conc.	20	Thin purple green bronze
Na-salicylate	conc.	25	No result—WO_3 does not dissolve
Na-succinate	conc.	25	Cathode somewhat dulled
Na_2S	250	40	Thin purple blue bronze
"Metso"	200	125	Thin shiny deposit—slightly blue
Borax	sat.	70	Purple green coloration
K-tartrate	150	60	Loose black deposit
Rochelle Salt	150	60	No deposit
Alkaline Agent	*Grams per liter*	*WO_3 grams per liter*	*Cathode appearance after electrolysis*
K-citrate	300	60	No deposit
Na_2WO_4	sat. 25°	70	No deposit
Na_2SnO_2	conc.	50	Thick granular deposit (Mostly Sn.)

Undoubtedly the WO_3 dissolves in these alkaline solutions as alkali tungstates. Of the baths shown in Table I. that made up of $Na_3PO_4.12H_2O$ plus WO_3 gave the best results. The "Metso" bath ($Na_2SiO_3.5H_2O$) gave nice deposits but they were badly contaminated with iron and consequently unsatisfactory. The other baths which gave no good deposits were greatly improved by being made strongly alkaline with 10% NaOH solution. Sodium benzoate, salicylate, and succinate, are but slightly alkaline and became acid to litmus when WO_3 was added. Potassium tartrate, rochelle salts and potassium citrate, should not be classified as alkaline agents.

In all the baths of Table I., WO_3 was the source of tungsten. Several baths were tried using $Na_2WO_4.2H_2O$ instead of WO_3. Saturated Na_2WO_4 alone gave no deposit but Na_2WO_4 added to a concentrated borax solution gave a thin, slightly shiny deposit. A concentrated Na_3PO_4 solution to which was added Na_2WO_4 also yielded a slight deposit.

4. *The $Na_3PO_4 + WO_3$ Bath*

The above mentioned work showed that the $Na_3PO_4 + WO_3$ bath gave the best results, so a study was made to find the conditions which yielded the greatest amount of deposit. The bath was made by dissolving the $Na_3PO_4.12H_2O$ (Baker and Adamson C. P.) in hot water, adding the weighed amount of WO_3 and heating until the solution was clear. This resulting solution, although clear, unless an excess of WO_3 was added, was always tinged yellow. During the addition of the WO_3, ammonia was constantly liberated due to the decomposition of the ammonium salts present in the WO_3 (General Chemical C. P.) by the alkaline solution. First a series of runs was made with a bath containing 350 grams per liter of the phosphate and varying amounts of WO_3. The results are shown in Table II.

TABLE II.

Effects of varying amounts of WO_3 in a phosphate bath (350 g. per 1.)

Temp. 90°C, current 11.1 amps. per sq. dm., time 15 min.

Added WO_3 grams per liter	*Cathode gain gram per sq. dm.*	*Appearance of the Cathode*
20	0.0011	purple red
40	0.0016	darker purple
60	0.0022	nice "silvery" deposit
80	0.0055	"silvery"—slight blue
100	0.0061	"silvery" more blue
120	0.0077	yellow red bronze
160	0.0066	dulled brass
200	0.0061	dulled brass

Then a series of runs was made using a more concentrated bath, 500 grams of $Na_3PO_4.12H_2O$ per liter, and varying amounts of WO_3. Conditions were kept the same. The results are shown in Table III.

TABLE III.

Effects of varying amounts of WO_3 in a phosphate bath. (500 grams per liter).

Temp. 90°C. current 11.1 amps. per sq. dm. time 15 minutes

Added WO_3 grams per liter	*Cathode gain grams per sq. dm.*	*Appearance of the Cathode*
20	no gain	some purplish bronze
40	0.0026	shiny blue red
60	0.0033	shiny—slight blue
80	0.0072	nice "silvery" deposit
100	0.0082	nice "silvery" deposit
120	0.0066	nice "silvery" deposit
160	0.0061	dulled brass
200	0.0066	dulled brass

In all cases the above solutions (Tables II. and III.) were made up fresh as they were needed. The results indicate that the bath should be made up in about the proportion 4 parts by weight of $Na_3PO_4.12H_2O$ to 1 part by weight of WO_3 in not too large volume of water. Another extremely concentrated phosphate bath was made up. It contained 300 grams of $Na_3PO_4.12H_2O$ and 100 grams of WO_3 in a total volume of only 400 c.c. This solution when electrolized for 20 minutes with 2.2 amps. per sq. dm. at 100°C yielded a cathode gain of 0.0305 gm. per sq. dm. but the deposit was very dull. A fresh solution of the same concentration electrolized with 10 amps. per sq. dm. gave no deposit. The above mentioned deposit was the thickest obtained from a phosphate bath but did not compare in appearance with the usual good "silvery" deposit of about 0.020 gm. per sq. dm.

In order to find the best current density, a bath was made up and used with different current densities. The bath contained

100 grams $Na_3PO_4.12H_2O$
30 grams WO_3
150 c.c. total volume

The results are shown in Table IV.

TABLE IV.

Effect of Current Density—Temp. 90° C, time 20 min.

Amps. per sq. dm.	*Cathode gain gram. per sq. dm.*	*Appearance of the Cathode*
9	0.0244	nice "silvery" deposit
20	0.0266	nice "silvery" deposit
42	0.030	nice "silvery" deposit

Lower current densities gave proportionately lower cathode gains. Undoubtedly the best current density is about 10 amps. per sq. dm., as the increased gain in weight does not warrant the larger increased current. Of course, the current efficiency in all these depositions is very low, much less than 1%—liberation of oxygen and hydrogen using most of the current.

Various metal cathodes were next tried with a phosphate bath containing 100 grams $Na_3PO_4.12H_2O$ and 18 grams WO_3 in a total volume of 200 c.c. (a fresh solution was used for each different cathode). The results are shown in Table V.

TABLE V.

Various cathodes used with a phosphate bath
Time 20 min. Temp. 90° C

Cathode used	*Cathode gain gram per sq. dm.*	*Appearance of the Cathode*	*Amperes per sq. dm.*
Brass	0.0082	"silvery" deposit	22.2
Cadmium	0.0072	dulled and darker	22.2
Copper	0.0082	"silvery" deposit	22.2
Chrom. steel	0.0085	no change	22.2
Iron	no gain	red purple bronze	21.1
Molybdenum	no gain	dulled somewhat	22.2
Nickel	0.0040	no change	22.2
Tin	no gain	no change	22.2
Tungsten	no gain	dulled somewhat	7.

The results in Table V. show that tungsten can be suitably deposited on brass, copper or chromium steel cathodes.

All the phosphate baths became nearly worthless after being used a few times and the yellow tinge of the fresh solution was completely gone. These old, used solutions gave only poor very thin colored deposits or merely a tungsten bronze on the cathode. Attempts to improve such baths by addition of various amounts of Na_3PO_4 or WO_3 or both were not successful. Table VI. shows the results of attempts to improve a bath—original bath containing 300 grams $Na_3PO_4.12H_2O$ and 100 grams WO_3.

TABLE VI.

Attempts to improve a phosphate bath
Brass cathodes, 5 amps. per sq. dm., time 30 min. temp. 90°

	Bath Composition	*Total Volume*	*Cathode gain Cell No. 1*	*Cell No. 2*	*Cathode Appearance*
A	Original	400 c.c.	0.0056 gm.	0.0054 gm.	dull brassy
B	A 100 gm.Na_3PO_4	550 "	0.0052 "	0.0051 "	dull
C	B+25 gm. WO_3	525 "	0.0029 "	0.0029 "	nice "silvery" dep.
D	C+75 gm.Na_3PO_4	650 "	0.0022 "	0.0020 "	nice "silvery" dep.
E	D evaporated	500 "	0.0014 "	0.0017 "	fairly good dep.
F	E boiled with H_2	500 "	0.0008 "	0.0008 "	thin poor dep.
G	F evaporated	275 "	0.0004 "	0.0003 "	thin streaked dep.

It is necessary to use hot solutions—no deposit being obtained from a cold bath.

The liberation of ammonia from the freshly made phosphate solutions suggested the use of ammonia and ammonium salts as addition reagents to increase the thickness of the metal deposit. Most of the deposits made were very nice in appearance but so thin as to furnish very little protection to the base metal. Thus, means of securing better deposits were necessary. In this

work the usual phosphate solution was used, with the two cells in series, one containing the addition reagent and the other serving as the control. Gain in weight of the two brass cathodes was recorded and difference in gain served as an index of the value of the added material. The results are recorded in Table VII. Conditions were maintained constant throughout.

TABLE VII.

Effect of the ammonium addition reagents on phosphate bath

Added Compound	*Result*
$(NH_4)_2\ CO_3$	no difference
NH_4Cl	no difference
$(NH_4)_2\ HPO_4$	less gain than control
$(NH_4)_2WO_4$	more gain than control
$P_2O_5.24WO_3+NH_4OH$	slightly more gain than control
$3NH_4OH.5WO_3$	brighter deposit than control

The experiments were merely qualitative in character and the observations made were nothing to warrant further study. Other added materials such as dextrose, potassium tartrate, rochelle salts, $KClO_3$ and NaCl were similarly tried with no particular improved result.

III. DISCUSSION

There is always the question as to whether or not this shiny metal deposit is really tungsten. When electrodeposited from a phosphate bath on a thin copper foil and dissolved in aqua regia, the tungsten is oxidized to the yellow insoluble WO_3. However the amount of WO_3 obtained by oxidizing the deposit was not as great as was expected from the amount of tungsten on the copper foil (that is the gain in weight of the cathode during electrolysis). The potential of a flat tungsten electrode (3 cm. x 6 cm. x .1 cm.) in N-KCl was .267 volts, that is the total combination

$$W\ (N\text{-}KCl)—Hg\text{-}Hg_2\ Cl_2\ sat. = .267\ volts$$

which was fairly stable, and the potential of the tungsten plated brass cathode in the same cell was fairly stable at .250 volt. This same potential was obtained from two cathodes, one plated from a carbonate solution and the other plated from the phosphate solution. All the deposits were so thin as to be immediately loosed from the base metal by HCl or HNO_3.

In all this work and in the work of Fink and Jones the deposits obtained were very thin. Seemingly a thin coating of the metal prevents any further deposition—a coated cathode gained only slightly (in weight) when used a second time in a new bath.

The cathode gain was about the same whether the run was made in 15 minutes or 2 hours. That the used bath was still good was proved by getting a shiny deposit on a new brass cathode. Perhaps the reason for these thin deposits is that tungsten will not plate on tungsten. When a flat tungsten cathode was used in the phosphate solution it was somewhat dulled but showed very slight if any increase in weight. Again this bath was proved satisfactory by plating on a brass cathode from the second cell run in series.

The platinum anodes used in all work were apparently unaffected by the solutions—showing absolutely no corrosion. In individual runs they did not lose weight. Other anodes used include copper which was not affected, cadmium which was blackened and corroded, tin which was also blackened and corroded, and tungsten which was corroded and covered with a loose black residue.

No very satisfactory method was found for measuring the alkalinity of the solutions used. The hydrogen electrode potentials were quite unstable and very poorly reproducible. Indicator methods also proved quite unsatisfactory. Of course the addition of the acidic WO_3 to the Na_3PO_4 solution decreased the alkalinity in proportion to the amount added. Table VIII. gives fairly satisfactory results obtained by means of the hydrogen electrode—results that at least indicate the general trend of the alkalinity of the solution. Various amounts of WO_3 were added to 100 c.c. parts of a saturated $NaPO_4$ solution, then the pH* measured and the solution was used as a bath for deposition on a brass cathode.

TABLE VIII.

Alkalinity of phosphate solutions and the resulting cathode deposits

Grams WO_3 added	*pH of soln.*	*Appearance of Cathode deposit*
0	12.5	no deposit
1	12.2	thin—"bronze"
2	11.6	thin—"bronze"
5	10.7	good—slightly blue
7	10.	very food shiny
10	9.2	nice deposit

* The designation pH is an unfortunate one. It is used here only because it has become fairly common practice to do so, and the practical worker would find it more familiar than if the alkalinity were expressed in grams of basic "OH" per liter as should really be done.

Theoretically the deposition of tungsten ought to be an easy matter. At any rate, it should be no more difficult than electrodeposition of other metals. In reality, we find that it is an exceedingly difficult thing to accomplish. At best but thin films of tungsten are obtainable so far as we know. There is no adequate explanation for this. Indeed the experimental studies convince the laboratory worker that we are still very far from an adequate explanation of the phenomena of electrodeposition. The solution of this question is wrapped up with the question of the nature of the metallic state itself. Once the latter is solved, it will no doubt point the way to a new electro-chemistry and fundamental improvements in practical electroplating and refining.

BRANCH NEWS

LOS ANGELES BRANCH

The regular monthly meeting was held October 12, 1932. President Ben Foss was sick and unable to attend so meeting was called to order by Vice-President M. D. Rynkofs.

Financial report and minutes of previous meeting were read and accepted. The Secretary read a letter to the Branch from Supreme President Mr. Van Derau. One of our members, Mr. Bartlett, who has been ill was reported improving.

In absence of Mr. Hurd, Mr. Marigold acted as Librarian.

The following questions were found in the box:

Question—How much gold must be added to gold solution to produce a hard plate, say in 5 minutes and at what temperature?

Answer—The amount of gold in solution has little effect on hardness. Add nickel to harden.

Question—What is the best anode for gold solution, carbon or gold?

Answer—Members did not agree, but several thought carbon anodes most economical.

Question—Does a gold solution keep well or should it be discarded periodically?

Answer—Should be discarded occasionally.

Question—What will prevent streaking in cyanide copper?

Answer—Add Rochelle Salts.

Question—What is best strip for die casting?

Answer—Sulphuric acid strip.

Minutes of the regular monthly meeting held November 9th, 1932, at the Rosslyn Hotel.

President Ben Foss presided.

Minutes of the previous meeting, and the financial report were read and accepted.

A letter from the Supreme President regarding the need of money for the Research Fund, was read. The Branch voted to have our member of the Research Committee, M. D. Rynkofs, send letters to the various manufacturers here to try and get subscriptions to the fund. Messrs. Rushton, Thornton, Kyle, and Francis were appointed as a committee to assist Mr. Rynkofs. The Branch voted to donate $10.00 to the fund immediately, with a promise of more to follow.

A bill for per capita tax was read and ordered paid.

The following members were suspended for non-payment of dues: Nichols, Kuss, Gibson, Caipo, Schill, Pinto, Pendlay, Dempsey and Bouslog. The Secretary was instructed to notify these members accordingly.

Mr. Hearst, the chemistry instructor, gave a talk on the plans of the chemistry class.

The meeting was turned over to the Librarian, Mr. Hurd.

The following questions were found in the box:

Question—Why does a brass solution plate red on cast iron when the same solution plates yellow on steel?

Answer—If cast iron has been pickled it often causes brass to plate red.

Question—What will take red spots out of cast bronze?

Answer—Pickle for 5 minutes in a hot pickle made up of 3 parts muriatic and one part sulphuric acid.

Question—How much hydrogen peroxide should be added to a nickel solution to stop pitting?

Answer—Any given amount.

Question—How can aluminum be treated to take a red color?

Answer—Anodic treatment. This is a patented process.

Question—Can aluminum be deposited electrically?

Answer—Yes, at very high temperature. Aluminum oxide is dissolved in a bath of molten cryolite. Carbon is used for both anode and cathode.

Mr. Hurd read a paper on Tungsten Plating.

Meeting adjourned.

EARL COFFIN, *Secretary-Treasurer*

WATERBURY BRANCH

Always an auspicious occasion, when George Hogaboom visits Waterbury Branch to deliver an address, Friday, October 14th, was no exception when George delivered an interesting talk on "The Progress of Electro-Plating".

The speaker prepared his talk with some reminiscent remarks of the formation of Waterbury Branch in 1921, and of which, he was the first President. Calling attention to the fact, that nearly all solutions had undergone changes the past few years, the speaker gave a recapitulation of what had been done along those lines. Suggested the reading of important papers in electroplating, at the Branch meetings. Heavy deposits and the conditions necessary to attain same, was touched on. Current density—hot nickel, single nickel salts and the deposition of rubber were also discussed. President Tennant Elwin expressed the appreciation of all present for the instructive remarks.

Despite the many attractions arranged for Armistice night, a goodly attendance was present at the November meeting to hear Ellsworth Candee, assistant Librarian of the local Branch, give an interesting abstract of a paper on "The Influence of Acidity in the Structure and Hardness of Electrodeposited Nickel" by MacNaughton and Hammond. A general discussion on the subject ensued, and a vote of thanks extended the speaker.

W. F. GUILFOILE, *Secretary*

NEWARK BRANCH

The Newark Branch held its regular meeting on Friday evening, December 2, 1932. When President Harrison called the meeting to order there were thirty-five members in attendance at the Elks Club, Broad St., Newark, N. J.

Communication from our Supreme President in regard to research work was received and Newark Branch voted to continue every effort backed by our Past Supreme President Sievering and A. J. Sizelove.

Communication from the Chicago Branch in regards to the Convention City, Chicago. Newark Branch members expect quite a delegation to Chicago.

After the regular business session, our Librarian, Mr. Samuel Taylor who started the unique method of reading some article or articles out of the Review at each meeting, read the article on Non-Adherence of Deposits. This article caused a real discussion and those members who have not read this article it starts the ball of discussion rolling.

Meeting adjourned at 10.45 P. M.

GEORGE REUTER, *Secretary*

BIGGER AND BETTER

Newark Knows How!

PLANT VISITS
EDUCATIONAL SESSION

We offer a new and unique educational program of interest to all

FLOOR SHOW AND DANCE
IN THE EVENING

Make this a day to be remembered as one of the days you really enjoyed. Renew friendship and make new friends.

April 22, 1933

SALAAM TEMPLE, NEWARK, N. J.

DANCE AND SHOW TICKETS, $1.00

BRIDGEPORT BRANCH

The Bridgeport Branch held its monthly meeting on October 7, at the Stratfield Hotel in the Chamber of Commerce Rooms. The fifteen members and six officers who were present, were called to order by Pres. Wagstaff at 8.15 P. M.

The only committee that had any report to make was the Sick Committee, which gave cheerful news of the recovery of Barney Moran.

Tom Chamberlain, Chairman of the program committee, presented a list of names of people who we might approach to ask them to lecture to our fellow-members at open meetings during the winter months.

The meeting adjourned at 9.45 P. M.

On Friday evening, November 4, the regular monthly meeting of the Bridgeport Branch was called to order by Bill Stratton.

Two very important communications were held over to the next meeting, hoping that there will be a greater number of members in attendance. These communications were those of Mr. Jacob Hay and Mr. O. Servis.

A motion was made and seconded that the future delegates to our conventions are to have the minutes of the convention published in book form and sent to the members, through a suggestion made by Roy O'Conner.

We are going to make an attempt to secure Mr. George Hogaboom to give us a lecture in December in the lecture room of the Stratfield Hotel.

The meeting adjourned at 10.00 P. M.

At 8.30 on December 2, the regular monthly meeting of the Bridgeport Branch was called to order. There were twenty members in attendance.

William Stratton exhibited a sample of Nickel, about which much discussion arose, and added to the interesting talk of Joe Downs on "Peroxide in Nickel Solutions."

Herman Brown, spoke on the "Volume of Peroxide used in Nickel Solution" and Mr. Ehrincrona also had a sample of work to show.

All of the members present took part in either asking questions or answering them, which proved very beneficial to all.

At 11 P. M. the meeting adjourned.

The Bridgeport Branch held their first open meeting of the season on Friday evening, December 9, in the lecture room of the Stratfield Hotel.

There were eighty-five members who came out for the meeting as the result of communications distributed by Ray O'Connor, Chairman, who obtained Mr. George Hogaboom to lecture to the members.

Mr. Hogaboom gave a most interesting talk on "Recent Developments In Electro-Plating Solutions." Due to long experience in this line, Mr. Hogaboom covered very clearly the advance of plating solutions from their very beginning to the present time.

The program committee is making an attempt to have similar open meetings each month, and it is our desire to have just as good a number of members in attendance at future meetings.

WM. FLAHERTY, *Secretary.*

ANDERSON BRANCH

The regular monthly meeting was held on October 3, 1932, and called to order at 7.45 P. M. by our President, Mr. Cleaver.

Roll call of officers showed Mr. Hammond absent.

A communication was read from Mr. Harlan, chairman of the Executive Committee of the Chicago Branch, regarding the publicity campaign for the next National Convention. All agreed that the Chicago Branch was doing everything in their power to put over a wonderful convention and that they could be assured of our hearty cooperation to urge our members to attend.

Another communication was read from Mr. M. R. Lorce, a member requesting that he be dropped from our organization. Motion presented and passed to suspend.

Another from our member, Mr. W. E. Sanders requesting us to change his address to Flint, Michigan. This request was handed by the Secretary.

Another from our Supreme President, Mr. C. Van Derau urging us to build up our membership and offering methods of so doing, to keep up the research work and to keep up our Monthly Review.

The final communication was from Mr. Walter Fraine, Secretary-Treasurer, A. E. S. Research Fund, requesting that we try and finish our payment to the Research Fund. This letter led to such discussion as we are now financially unable to pay. However, we are over $100 behind in our dues, so a committee consisting of the Board of Managers, Mr. Guy Cole, Mr. C. Wilson, and Mr. F. Hammond was appointed to assist the Treasurer in collecting the dues. Further Mr. Cleaver appointed himself and Mr. G. S. Cole as a committee to approach the bank to try and recover all or some of the $185.00 we lost when the bank failed. With the enthusiasm shown we feel that we should soon be able to wipe out this debt.

Bills for Convention Report, Constitutions, Applications and per capita tax were ordered paid and warrants drawn.

There were no applications for new members.

The discussion then led to methods of having turnout as we had last year. A committee composed of Mr. W. Castell, Mr. Kaegi, Mr. Wagner, and Mr. Guy Cole was appointed as a program committee—they to arrange a speaker for each meeting. This committee will meet Thursday night, Oct. 6th, for discussion.

Further it was decided to have a "Kitty", each member present at the next meeting to deposit 5 cents and at the end of the meeting everyones name in the Branch Society will be placed in a hat and a name drawn—if he were there he would win all the money in the hat. We felt that this might be some incentive together with a good speaker to increase attendance.

The meeting adjourned at 9.45 with everyone agreeing that next week he would make a special effort to bring out another member so that we would be sure and show the program committee we were behind them.

Regular monthly meeting held at the Anderson Hotel, Monday evening, November 7, at 7.30 P. M.

The meeting opened with the introduction of Dr. G. L. Bray, Professor of Metallurgy of Purdue University as our speaker for the evening. Dr. Bray

talked on the "Fundamentals of Electro-deposition". He confined his talk to one hours' duration as he was unable to spend any more time with us, due to another appointment. As a result we regretted his having to leave as we were unable to ask many questions. Nevertheless, he gave a very interesting talk relative to the explanation of plating terms which we constantly come in contact with.

Following his talk the business meeting opened with all officers present.

Communication was read from our Supreme President regarding the research problem, whereupon the branch voted immediate payment of our amount due plus one dollar extra per member to the Research Fund.

The second of a series of articles from the Chicago Branch relative to the 1933 Convention was read.

The above were the only communications and there were no bills.

For the good of the organization it was suggested that the Supreme secretary be notified of a special meeting which the Branch held Wednesday Evening, October 26, 1932 at the Y. M. C. A. We had the pleasure of listening to Mr. Richard Schneiderwind, Research Engineer, University of Michigan, who gave us a very interesting talk of the History of Chromium Plating. Mr. Schneiderwind spent the evening with us and answered many questions of interest to all.

The branch acted and suspended Mr. E. L. Props, and accepted the resignation of Mr. E. A. Rhodes.

Mr. Guy Cole was called upon to tell us of his progress as chairman of the delinquent dues committee.

Mr. Castell was called upon to tell us of the activities of the program committee. Thereupon much discussion resulted as to whether we should have open meetings. It was finally agreed that we should have one regular meeting per month with the second meeting subject to call. For our regular meetings we have arranged a speaker for every meeting from now 'till March. The call meeting to be in the form of plant visitations or special business. The program committee has made several arrangements for plant visits.

The matter of several of our members failing to show up for meetings brought up some comments as we have done all we can to make the meetings interesting.

As a result the Secretary was instructed to be sure all notices were mailed by Wednesday preceding the meeting.

Finally the "Kitty" was collected and Mr. Guy Cole was the lucky winner.

Meeting adjourned at 10.00 P. M.

G. S. Cole, *Secretary.*

DETROIT BRANCH

The regular monthly meeting Detroit Branch A. E. S. was held in Hotel Statler, Friday evening, October 7th. President J. H. Hansjosten presiding. Minutes of the previous meeting were read and approved, after the regular order of business, communications and bills.

There being no further business, the speaker of the evening, Mr. R. E. Pettit, Sales Engineer, Aluminum Colors, Inc., was introduced. Mr. Pettit

presented a very interesting talk on, Alumilite Anotic Treatments and Colors of Aluminum. A variety of samples and colors were also displayed. Discussion was invited and several questions were asked, which Mr. Pettit answered.

The November Meeting was promised to be very educational, combined with smokes and a lunch, after which meeting adjourned.

CHAS. E. MARKER, *Secretary-Treasurer.*

HARTFORD-CONNECTICUT VALLEY BRANCH

Hartford-Connecticut Valley Branch held its first Fall meeting on Monday evening, September 26, 1932, at the Hartford Chamber of Commerce, 805 Main St., Hartford, Conn.

The meeting was called to order at 8.30 P. M. with President Fleming in the chair. Minutes of the previous meeting were read and accepted. Bills amounting to $32.50 were voted paid. Communications were read and placed on file. One application for active membership was received and voted upon to take the usual course. The applicant was Mr. Anthony Bruno of the Wm. Gilbert Clock Co., of Winsted, Conn. One transfer, Mr. A. A. Brunnel of the Worcester Branch, was received and accepted.

Mr. Geo. B. Hogaboom was the speaker for the evening, and gave a very interesting and instructive talk on the advancement made, in recent years, in the methods of electroplating. His talk covered practically all of the common metals, and the modern practice of plating them. In conclusion he was given a hearty rising vote of thanks.

The meeting was attended by twenty-six members and adjourned at 10.45 P. M.

The October meeting was held on Monday evening, October 24, at the Springfield Chamber of Commerce, Springfield, Mass.

The meeting was called to order at 8.30 P. M. with President Fleming in the chair. Minutes of the previous meeting were read and accepted. No bills were presented. All communications were read and placed on file.

Much discussion followed the reading of various letters. The discussion was mostly in regards to the financing of our research work as well as the "Review".

Mr. Anthony Bruno was elected as an Active member.

There being no speaker for the evening, the meeting was adjourned at 10.30 P. M.

V. E. GRANT, *Secretary.*

CHICAGO BRANCH

The regular monthly meeting was held Saturday, December 10, 1932. President F. J. Hanlon presiding and all officers present.

We had a very large attendance—45 members. The speaker of the evening was Dr. Hugo Diemer, Industrial Engineer, lectured on "What a foreman should know about *Management.*"

It is with deep regret that we announce the sudden death of our fellow member, Mr. S. E. Huenerfauth.

Our Convention Committee Reports progress. No effort is being spared that will make our 1933 Convention one long to be remembered.

Our Educational Committee wishes to assure you that papers they are selecting to be read and discussed, during the Convention will be of a higher practical value to the plater.

Chicago Branch invites you to attend our Booster meeting and smoker.

All members in the vicinity of Chicago are invited to drop in.

This smoker is being held in place of our annual banquet.

E. G. STENBERG, *Secretary*

PITTSBURGH BRANCH

Our October meeting was held on Friday evening, October 7th, in the Keystone Club, and in the shape of a dinner party. The attendance was small, but there was plenty of good fellowship which we trust will develop in a manner that will make our future meetings better attended. We expect to put every member on the list of speakers, in other words, every member will have an opportunity of getting on his feet and telling his fellow workers all about the work he is doing, and if he has a problem, to go into it in detail, in order that other members can be of assistance to him. Pittsburgh Branch, in order to be of as much help possible to the research committee, promptly ordered the secretary-treasurer to send a check of $56.00 to treasurer Walter Fraine, to help the Research Committee to carry on the work at Washington, we all wished that we could afford to send a larger sum. The members are very much interested in the exposure tests of plated samples on the racks at Brunots Island, and we have had several who requested an opportunity of going on the trips of inspection.

Our November meeting was held on Friday evening, November 4th, in the Keystone Club, where all future meetings will be held, and it was mentioned that the Editor to please note and make the change in meeting place in the Monthly Review. Our attendance was not so large this evening, but after we had taken care of the usual business matters, President Peter, turned the chair to the speaker of the evening, who gave us a surprise talk on the chromium plating situation and pointed out his views of the recent developments in the patent decision. It was evident that much time and effort had been spent to put this into common language, and was given a hearty vote of thanks. Our speaker selected for our December meeting will be none other than the ever popular member Wilfred S. McKeon, he will choose his own subject, and we are looking forward to our December meeting with interest. Mr. McKeon has just returned from an extended trip to Europe, and there is no doubt he will tell us of the many interesting things he saw in the plating industry in a foreign field.

S. E. HEDDEN, *Secretary-Treasurer.*

DAYTON BRANCH

The regular monthly meeting of Dayton Branch was held at the Y. M. C. A. Saturday evening, October 1st, 1932, with our President Mr. Cusick, presiding.

The business session included the reading of a communication from the Supreme President, Mr. Van Derau also one from Mr. Gilbertson and one from Chicago Branch.

Mr. Van Derau who is a member of Dayton Branch was present and gave a very interesting and inspiring talk in which he stressed the need for continuing the work of the Bureau of Standards as it is now in the most vital stage; he also told of plans now under way to consider ways and means of making the "Review" a monthly publication instead of quarterly as is now the case, and which we feel sure would meet with the hearty approval of all members.

Mr. Van Derau was followed by Mr. Fraine, Secretary and Treasurer of the Research Fund, who also told of the work being done at the Bureau of Standards and the great need for carrying on this work.

Dayton Branch is planning a very interesting and educational program for the coming winter, in fact, it is our desire to make these meetings so interesting and educational that no one will want to miss any of them.

WARD B. PROTSMAN, *Secretary-Treasurer.*

CLEVELAND BRANCH

The monthly meeting of the Cleveland Branch was called to order by President E. Steen Thompson. The minutes of the November meeting were approved as read. Our Librarian, Mr. Nachtman has good programs for the meetings and the attendance is very good of late, and we hope and wish that it will be better.

H. A. WEBER, *Secretary.*

BOSTON BRANCH

Boston Branch met Thursday the 1st at the American House with President Hardy in the chair.

After the regular order of business the meeting was turned over to the Librarian, who presented the speaker of the evening, Mr. Frank Clarke, whose subject was "What is the Correct P. H. of the Nickel Solution". He spoke for more than one hour and was very interesting and a vote of thanks was given Mr. Clarke for his talk. He answered all questions and there was also a good discussion that lasted until the meeting adjourned at 10.30 P. M.

Boston Branch met Thursday, October 6th at the American House, with President Hardy in the chair.

After the regular order of business which was very short owing to the lack of attendance, Mr. Charles F. Campbell gave a short talk on the discovery of the different plating solutions. This was brought about through a mistake made in dates at the last meeting by Mr. Campbell and it was very interesting as some of the members never knew it. The communication of the program committee was turned over to Mr. Mackie our Librarian. A discussion on Mr. Campbell's talk lasted one hour. Meeting adjourning at 10.15 P. M.

A. W. GARRETT, *Secretary.*

ST. LOUIS BRANCH

The regular meeting of St. Louis Branch was called to order by President Al. Barth, at 2822 La Salle St., on October 14th. Roll call of officers showed one absent. One application was received and turned over to the Board of Managers, to be passed on at the next meeting.

One member suspended.

The meeting was then placed in charge of Librarian F. P. Meninges who handed out Question cards and every one was turned in with a Question and a Discussion started, which was very interesting. And then Dr. Stout of Washington University gave us an instructing talk on Cadmium Plating, and there were also some samples of Cadmium Plating on Malleable Iron, showing black spots after storing for some months.

Meeting adjourned at 10.10 P. M.

Some of the old timers came to the meeting. Hope to see you often, as we like to hear what you are doing. So try and come around.

The November meeting of the St. Louis Branch was held on Friday, November 11th. The Roll Call of officers showing two absentees. The minutes of the previous meeting were read and approved. The "Booster Letter" from Chicago giving much information regarding the 1933 Convention was read. A letter from President Van Derau in reference to Research was also read. Mr. B. Daw's application for membership was approved and he was elected. In the absence of Mr. Musick, Mr. Williams made a report on the Research Committee and a motion made and carried that the St. Louis members render Mr. Musick all possible aid.

The meeting was then turned over to the Librarian who asked for questions, after these were answered some samples were shown and the cause of peeling of chrome plating pieces and the remedy were discussed. Dr. Stout of Washington University then gave us a talk which proved very interesting.

CHAS. T. MCGINLEY, *Secretary.*

HARTFORD-CONNECTICUT VALLEY BRANCH

The Hartford-Connecticut Valley Branch of the A. E. S. held their regular monthly meeting on Monday evening, November 28, at the Hartford Chamber of Commerce, Hartford, Conn.

The meeting was called to order at 8.30 P. M. with President Fleming in the chair. Minutes of the previous meeting were read and accepted. One bill for our 2nd Quarter P. C. T. amounting to $22.05 was voted paid. All communications were read and discussed.

There being no speaker for the evening, time was spent in discussing ways and means of obtaining new members, and also some way of increasing the financial strength of the Branch.

The meeting was attended by only ten members and was adjourned at 10.00 o'clock.

V. E. GRANT, *Secretary.*

APPLICATIONS

MR. DANIEL BAUMANN, 268 Nesbit Terrace, Irvington, N. J. ..... Newark
MR. VINCENT PISCHL, 94 Jacoby St., Maplewood, N. J. ..... Newark
MR. JOHN BERTGLUN ..... Newark
ARTHUR WALLACE, 209 W. 38th St., New York City ..... New York
WALTER E. WRENN, 1706 Shephard St., Windsor, Ontario ..... Detroit
R. E. SMITH, 2726 West 24th St., Erie, Pa., R.F.D. No. 2 ..... Cleveland
L. A. DAVIES, 205 Wacker Drive, Chicago, Ill., (Assoc.) ..... Chicago
R. F. McGUIRE, 205 Wacker Drive, Chicago, Ill., (Assoc.) ..... Chicago
JOHN D. LEE, 13610 Pinwhist Ave., Detroit, Mich. ..... Detroit
ANTHONY BRUNO, 86 Culvert St., Torrington, Conn. ..... Hartford
MELBERT C. MILLER, 357 South Queen St., Lancaster, Pa. ..... Philadelphia
BURTON G. DAW, 2822 La Salle St., St. Louis, Mo., (Assoc.) ..... St. Louis
ARNOLD OPPENHEIM, Chatham, N. J., (Assoc.) ..... Newark
DR. MOSSIMO OLIVETTI, c/o J.C.Olivetti Co.,Jurea, Italy (Assoc.) .. New York
ELWOOD GURMANN, 360 Pennington Ave., Trenton, N. J. ..... Philadelphia

ELECTIONS

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